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Reactions of 1,10-phenanthroline with hydrogen, cadmium and zinc ions

Michael John Fahsel
Iowa State University

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HYDROGEN, CADMIUM AND ZINC IONS.

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REACTIONS OF 1,10-PHENANTHROLINE
WITH HYDROGEN, CADMIUM AND ZINC IONS

by

Michael John Fahsel

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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Of Science and Technology
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1965

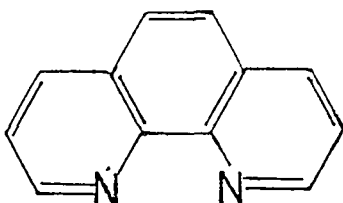
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I. INTRODUCTION

The compound 1,10-phenanthroline, P, is a bidentate ligand with the following structure



It reacts with many transition metals, M^{+Z} , forming MP_3^{+Z} octahedral complexes. Its principal utility has been as a ligand for the spectrophotometric determination of trace quantities of iron(II). The FeP_3^{+2} complex has also been very useful as an oxidation-reduction indicator. These and other uses of 1,10-phenanthroline are further described in review articles (10,63).

Many substituted 1,10-phenanthroline compounds have been prepared. This family of compounds all having the same ferriin function group, $-C=N-C-C-N=C-$, have been studied by many workers. The effect of these substituents on ligand properties like basicity, solubility, wavelength of maximum absorbance and steric hindrance to complex formation has been studied. Further, the effect of substituents on the properties of the resulting FeP_3^{+2} complex such as the pH for

optimum color development, molar absorptivity, oxidation-reduction potential and extractability has been investigated (10,54,63).

A. Purpose of This Work

The purpose of the present work has been to investigate the reaction between hydrogen ion and 1,10-phenanthroline with a specific interest in the poly(1,10-phenanthroline)hydrogen (I) species reported by Grimes (24) and Fullerton (20). In a broader sense this has involved gathering experimental evidence to show the existence of nonexistence of these species. Should the evidence indicate that these species do exist then it would be of interest to determine the over-all formation constants for the various species. Further, since such higher order species, HP_2^{+1} and HP_3^{+1} , would seem to violate existing thoughts about the possible stoichiometries for a hydrogen ion, it would be of interest to speculate one or more plausible structures.

II. LITERATURE REVIEW OF THE HYDROGEN ION AND 1,10-PHENANTHROLINE REACTION

The dissociation of an acid, HB, may be represented by the following reaction,



and the acid dissociation constant, K_a , is

$$K_a = \frac{(\text{H}^{+1})(\text{B})}{(\text{HB}^{+1})} \quad (2)$$

and

$$\text{p}K_a = \text{pH} + \log \frac{(\text{HB}^{+1})}{(\text{B})} . \quad (3)$$

The acid dissociation constant of mono(1,10-phenanthroline)hydrogen(I), HP^{+1} , has been measured by several workers. The results are summarized in Table 6. The most commonly used technique has entailed measuring the pH of a partially neutralized solution of 1,10-phenanthroline. Then assuming a 1:1 stoichiometry the concentration of HP^{+1} , (HP^{+1}) , may be determined from the difference between the total concentration of hydrogen ion added, (H_T^{+1}) , and the concentration of uncombined hydrogen ion, (H^{+1}) , that is measured experimentally,

$$(\text{HP}^{+1}) = (\text{H}_T^{+1}) - (\text{H}^{+1}) . \quad (4)$$

Further, the concentration of unreacted 1,10-phenanthroline may be determined from

$$(\text{P}) = (\text{P}_T) - (\text{HP}^{+1}) . \quad (5)$$

Hence, the $\text{p}K_a$ may be readily determined from a single pH

measurement using Equation 3. Most commonly the pH measurement is made when about one half of the base, 1,10-phenanthroline, has been neutralized. This basic method has been employed by several workers to determine the pK_a value for HP^{+1} .

Hawkins et al. (25) determined the pK_a values for 1,10-phenanthroline and several "pyridine" ring substituted 1,10-phenanthrolines.

The potentiometric technique was modified somewhat by Brandt and Gullstrom (11) to determine the acid dissociation constant of several 5-substituted or "benzene" ring substituted 1,10-phenanthrolines. Because of the low aqueous solubility of these substituted 1,10-phenanthrolines, they employed a water-dioxane solvent system. The relative acid dissociation constants were determined as a function of the volume percentage of dioxane. The aqueous pK_a values were determined from a plot of relative pK_a vs. percentage dioxane by extrapolation to zero percent dioxane.

Schilt and Smith (50) employed the same basic procedure used by Brandt and Gullstrom (11) to determine the pK_a values of forty substituted 1,10-phenanthrolines.

Another procedure which has been employed by other workers involves a spectrophotometric technique. The uncombined base, 1,10-phenanthroline, has two strong absorption peaks in the ultraviolet region at about 265 and 229 $m\mu$. Upon protonation in acidic medium, these peaks are shifted

to about 272 and 220 $m\mu$ respectively (37). The pK_a value for 1,10-phenanthroline can be calculated from the simultaneous solution of the following two equations,

$$(P_T) = (P) + (HP^{+1}) \quad (6)$$

$$A = \epsilon_P b(P) + \epsilon_{HP^{+1}} b(HP^{+1}) \quad (7)$$

which gives

$$\frac{(HP^{+1})}{(P)} = \frac{\epsilon_P(P_T) - A}{A - \epsilon_{HP^{+1}}(P_T)} \quad (8)$$

where A is the absorbance of the solution containing both the uncombined base and the protonated base, ϵ_P and ϵ_{HP} are the molar absorptivities of the uncombined base and the protonated base at the wavelength where A is measured and b is the cell path in centimeters. The ratio of protonated base to uncombined base is generally altered by employing several buffer solutions of known pH.

An alternate spectrophotometric technique similar to the one above involves the determination of the overall molar absorptivity of a peak where both the uncombined base and protonated base absorb. The pK_a value may be determined from the inflection point of a plot of molar absorptivity vs. pH.

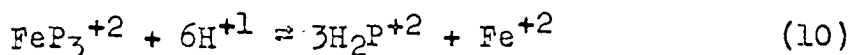
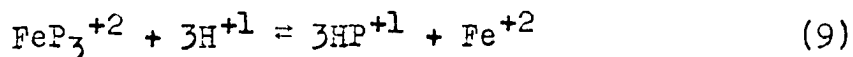
The former spectrophotometric technique was employed by Lahiri and Aditya (35). They reported a pK_a of 4.95. The total concentration of 1,10-phenanthroline used in their study was 2×10^{-5} M. The latter spectrophotometric technique was employed by Linnell and Kaczmarczyk (37). Their reported

pK_a was 5.47.

Lee, Kolthoff and Leussing (36) have extensively investigated the reaction between hydrogen ion and 1,10-phenanthroline. They concluded that although 1,10-phenanthroline has two basic nitrogen atoms it behaves as a monoacidic base.

They conducted a potentiometric titration of 0.01 M 1,10-phenanthroline with 0.2 M hydrochloric acid. An experimental plot of pH vs. moles of acid added per mole of 1,10-phenanthroline was prepared. The experimental points were compared with a theoretical curve calculated from their previously determined acid dissociation constant for the HP^{+1} species. They point out that the agreement between the experimental points and the theoretical curve is good. There is a substantial break in the curve at a 1:1 ratio of acid to 1,10-phenanthroline but little change in pH is observed in the region corresponding to a 2:1 ratio.

Secondly, they investigated the reaction between hydrogen ion and tris(1,10-phenanthroline)iron(II), FeP_3^{+2} . Two possible reactions were speculated,



that is, the dissociation of FeP_3^{+2} in acidic medium to form either HP^{+1} or H_2P^{+2} . The equilibrium constants, K , for the two reactions are

$$K_1 = \frac{(Fe^{+2})(HP^{+1})^3}{(FeP_3^{+2})(H^{+1})^3} \quad (11)$$

$$K_2 = \frac{(\text{Fe}^{+2})(\text{H}_2\text{P}^{+2})^3}{(\text{FeP}_3^{+2})(\text{H}^{+1})^6} . \quad (12)$$

Solutions were prepared wherein the total concentrations of iron(II), hydrogen ion, and 1,10-phenanthroline were known. The equilibrium concentration of the colored FeP_3^{+2} complex was determined spectrophotometrically. Assuming that the concentrations of uncombined 1,10-phenanthroline, FeP_1^{+2} and FeP_2^{+2} are negligible, the concentrations of all the parameters in the system can be determined from

$$(\text{Fe}^{+2}) = (\text{Fe}_T^{+2}) - (\text{FeP}_3^{+2}) \quad (13)$$

$$(\text{HP}^{+1}) = (\text{H}_T^{+1}) - 3(\text{FeP}_3^{+2}) \quad (14)$$

$$(\text{H}_2\text{P}^{+2}) = \frac{(\text{H}_T^{+1}) - 3(\text{FeP}_3^{+2})}{2} . \quad (15)$$

The equilibrium constants for the two hypothetical reactions were determined at several different total concentrations of iron(II), hydrogen ion and 1,10-phenanthroline. The total variation in K_1 was from 1.8 to 8.4×10^{-7} while that for K_2 varied by a factor of about a million. They concluded that this was strong evidence that 1,10-phenanthroline is a monoacidic base. It should be noted that the concentration of uncombined 1,10-phenanthroline in their solutions was about 10^{-7} M.

Lee et al. (36) also performed a conductometric titration of 0.01 M 1,10-phenanthroline with 0.2 M hydrochloric acid using freshly platinized electrodes. The resulting plot

of conductance vs. moles of acid added per mole of 1,10-phenanthroline had a distinct endpoint indicating a 1:1 interaction.

Upon considering this experimental evidence Lee et al. (36) concluded that although 1,10-phenanthroline has two basic nitrogen atoms it behaves as a monoacidic base. They concluded further that the nitrogen atoms are separated by a distance of only $2.5 \overset{\text{O}}{\text{\AA}}$ and they occupy such positions in the molecule that electrostatic or steric forces or both prevent two hydrogen ions from combining with 1,10-phenanthroline.

Later workers have shown spectrophotometric evidence in the ultraviolet region for the existence of diprotonated 1,10-phenanthroline, H_2P^{+2} , in strongly acidic solution. Margerum et al. (41) have determined the molar absorptivity of an absorption peak at $277.5 \text{ m}\mu$ as a function of the pH of the solution. They calculated a pK_a value of -0.70 for the diprotonated species. They suggest that the diprotonated species begins to form in solutions more acidic than 1 M HClO_4 . In a similar manner Linnell and Kaczmarczyk (37) determined a pK_a value of -1.6 in concentrated sulfuric acid solution.

No complete description of the bonding in mono(1,10-phenanthroline)hydrogen(I) was found in the literature. However 2,2'-bipyridine which also contains the ferroin functional group has been studied more extensively. It, like

1,10-phenanthroline, behaves as a monoacidic base except in strongly acidic solution. Baxendale and George (6) have suggested that 2,2'-bipyridine does not add a second proton because hydrogen bonding stabilizes the monoprotonated species.

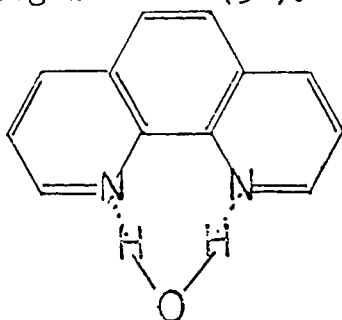
The importance of hydrogen bonding in compounds containing the ferroin group has been disputed by other workers. Westheimer and Benfey (64) have theoretically derived an upper limit to the effect of hydrogen bonding of some dibasic acids based on the ratio of K_{a1} to K_{a2} . They determined the K_{a1} and K_{a2} for the diprotonated 2,2'-bipyridine and from the magnitude of the ratio of K_{a1} to K_{a2} they concluded that hydrogen bonding in monoprotonated 2,2'-bipyridine is insignificant.

Nakamoto (44) has investigated the infrared spectrum and nuclear magnetic resonance spectrum of the solid hydrochloride of 2,2'-bipyridine and no positive evidence for $N-H\cdots N$ hydrogen bonding was found. They concluded that the $H\cdots N$ distance, 2.60 \AA , was too long for adequate hydrogen bonding.

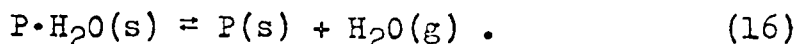
In conclusion, one must use caution in comparing 1,10-phenanthroline and 2,2'-bipyridine because the former compound is rigidly planar while the latter compound has free rotation of the two "pyridine" rings altering the alignment between the two ring nitrogen atoms.

Many 1,10-phenanthrolines form solid hydrates. These are definite compounds having characteristic melting points.

They lose their water at a characteristic temperature. The parent 1,10-phenanthroline crystallizes from water as the monohydrate, 1,10-phenanthroline-1-water. Infrared studies indicate that the water is bonded to 1,10-phenanthroline by two $O-H\cdots N$ hydrogen bonds (54).



Fritz et al. (19) have measured the dissociation pressure at several temperatures for the reaction

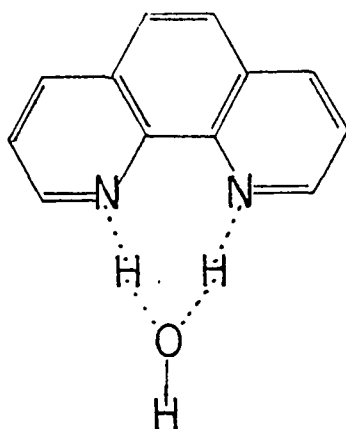


From the data they calculated the average strength of the two hydrogen bonds in 1,10-phenanthroline-1-water. A value of 7.25 kcal./mole for a single $O-H\cdots N$ hydrogen bond was reported. This compared favorably with hydrogen bond strengths reported for acetic and formic acids.

Nakamoto (44) has reported the preparation of 1,10-phenanthroline monohydrochloride monohydrate. This was prepared by passing gaseous hydrogen chloride into an ethereal solution of 1,10-phenanthroline (monohydrate?). The product was dried for five days in a phosphorus pentoxide desiccator. An elemental analysis of the material indicated the above compound.

Beattie and Webster (7) have prepared 1,10-phenanthro-

line monohydrate monohydrochloride in a similar manner. These authors specifically stated that they started with solid 1,10-phenanthroline-1-water. They propose a structure consisting of a hydronium ion which is bonded to 1,10-phenanthroline by two O...H...N hydrogen bonds for the cation of 1,10-phenanthroline monohydrate monohydrochloride.



They suggest that hydrogen bonding would be of importance in determining the base strength of the monohydrochloride in aqueous solution.

To show the existence of 1,10-phenanthroline-1-water in solution Beattie and Webster (7) compared the infrared spectra of solutions of 1,10-phenanthroline-1-water in ether and in benzene in a region where the anhydrous 1,10-phenanthroline does not absorb. In the ethereal solution the spectra of water and 1,10-phenanthroline-1-water were

identical indicating complete dissociation of 1,10-phenanthroline-1-water to water and 1,10-phenanthroline. In benzene the free water peaks in the solution of 1,10-phenanthroline-1-water are considerably smaller than those expected from complete dissociation. Further, there is a new, broad peak centered at about 3410 cm^{-1} which is analogous to that found for the solid 1,10-phenanthroline-1-water. These results indicate that in the benzene system there is only partial dissociation of 1,10-phenanthroline-1-water while in the more polar ethereal solvent there is complete dissociation.

Some recent workers have determined the thermodynamic quantities ΔH , ΔS and ΔF for the neutralization reaction of 1,10-phenanthroline. Nasanen and Uusitalo (45) determined the acid dissociation constant potentiometrically at 0° , 25° and 50°C . From the temperature dependence of the acid dissociation constant the heat of formation of mono(1,10-phenanthroline)hydrogen(I) was calculated to be -3.5 kcal./mole . The entropy change for the reaction was calculated to be 10.2 e.u.

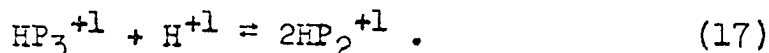
Kul'ba and Makashev (34) have studied the reaction calorimetrically and have determined values of $\Delta F = -7.0\text{ kcal./mole}$, $\Delta H = -4.6\text{ kcal./mole}$ and $\Delta S = 8\text{ e.u.}$ In a similar manner Anderegg (2) has determined values of $\Delta F = -3.95\text{ kcal./mole}$, $\Delta H = -6.6\text{ kcal./mole}$ and $\Delta S = 9.2\text{ e.u.}$

Lahiri and Aditya (35) have reported values of $\Delta F = -6.90\text{ kcal./mole}$, $\Delta H = -4.07\text{ kcal./mole}$ and $\Delta S = 9.5\text{ e.u.}$

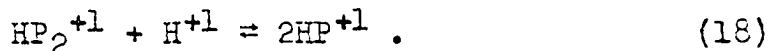
These were determined from the temperature dependence of the spectrophotometrically determined acid dissociation constant.

To date Grimes (24) and Fullerton (20) have been the only workers to suggest the existence of poly(1,10-phenanthroline) hydrogen ion species. Both workers have determined the over-all formation constants of the HP_1^{+1} , HP_2^{+1} and HP_3^{+1} species using the Ag/AgP_2NO_3 electrode. This same basic technique has been employed by the present author and it will be described in considerable detail below. The values reported for the logarithm of the over-all formation constants are 5.05, 8.40 and 10.3 (24) and 5.27, 8.10 and 12.07 (20).

Grimes (24) cited further evidence for the existence of the poly(1,10-phenanthroline)hydrogen(I) species. He performed a conductometric titration of hydrochloric acid solutions which were saturated with 1,10-phenanthroline using hydrochloric acid as the titrant. At the beginning of the titration \bar{n} was greater than two indicating that some of the HP_3^{+1} species was initially present. This species would be titrated first



When the HP_3^{+1} species was depleted a slight break in the plot of conductance vs. volume of titrant was observed. Next the HP_2^{+1} species would be titrated



Thereafter a second, sharp break was observed due to the conductance of the excess hydrogen ion. The sharpness of the

first break increased as the total concentration of 1,10-phenanthroline in the system was increased. The total concentration of 1,10-phenanthroline could be increased by using a more concentrated initial hydrochloric acid solution.

Grimes (24) also noted the abnormally high solubility of 1,10-phenanthroline in aqueous acidic solution. This high solubility could not be accounted for by assuming only the HP_1^{+1} species. However by assuming contributions to the solubility by HP_2^{+1} and HP_3^{+1} the abnormally high solubility could be explained. Some solubility studies have been conducted in the present work and this area of investigation will be more thoroughly pursued below.

Dale (14) did some preliminary work with the Ag/AgP_2NO_3 electrode system in an attempt to further elucidate the higher order HP_n^{+1} species. He encountered problems in the preparation of reproducible electrodes and discontinued the study of the Ag/AgP_2NO_3 electrode in favor of a competitive technique employing silver as the competing ion. A silver electrode was used as the indicating electrode. By this method the over-all formation constants of some transition metal-1,10-phenanthroline complexes were determined. Using this same technique he performed a titration of hydrogen ion with 1,10-phenanthroline. However, from his data he was unable to make a conclusion concerning the existence of the higher order HP_n^{+1} species.

III. MATHEMATICAL COMPUTATION OF FORMATION CONSTANTS

A. General Considerations

In the study of a metal-ligand system some general, commonly used concepts are employed. The book by Rossotti and Rossotti (49) may be consulted for a more complete treatment.

In the general reaction between a central metal ion, B, and a ligand, A, several mononuclear metal-ligand species, BA_n , may be formed.



The over-all stoichiometric formation constant, β_n , for the BA_n species is defined as

$$\beta_n = \frac{(BA_n)}{(B)(A)^n} \quad (20)$$

where the terms in brackets are equilibrium concentrations. For convenience ionic charges will be omitted in this treatment. Thermodynamic constants are ones employing activities rather than concentrations of the metal, ligand and BA_n . Normally the thermodynamic constants are not determined for several reasons. It would be necessary to know the activity coefficients of all the ionic species in the system to convert the stoichiometric formation constants to thermodynamic ones. In many cases the activity coefficients are not readily available. Thermodynamic constants could be obtained by extrapolating to infinite dilution stoichiometric formation constants which have been determined at several different

ionic strengths. This technique is tedious and is not usually done.

More frequently the activity coefficients are rendered constant by employing a medium of constant ionic strength. The stoichiometric formation constants thus obtained are valid for that specific ionic strength. Formation constants reported in this manner are often as useful as thermodynamic ones.

To control the ionic strength a significantly large concentration of an ideally noninteracting salt is employed. In practice this noninteracting stipulation rarely exists. Further, interactions of the metal or ligand with materials which are used to control other medium parameters, such as the pH, are often encountered. When these interactions or competing reactions are known to exist the formation constant obtained is the over-all conditional formation constant, β'_n ,

$$\beta'_n = \frac{(BA_n)}{(B')(A')^n} \quad (21)$$

where (B') is the total concentration of metal not bound to the ligand and (A') is the total concentration of ligand not bound to the metal. Hence, conditional formation constants are a function of the concentration of any interacting components in the medium.

Some other concepts are often used when describing metal-ligand systems. The step formation constant for the BA_n species, K_n , which is the equilibrium constant for the

reaction,



is defined as

$$K_n = \frac{(BA_n)}{(BA_{n-1})(A)} \quad (23)$$

The over-all formation constant for the BA_n species is the product of the n step formation constants.

B. The Computation of Formation Constants

Many methods are available for the computation of formation constants. The book by Rossotti and Rossotti (49) and the review articles by Sullivan and Hindman (57) and Rossotti and Rossotti (48) describe and illustrate several of these methods. Several methods will be mentioned here to illustrate the scope of these computational techniques.

In a metal-ligand system the total analytical concentration of ligand, A , may be expressed by

$$A = a + \sum_{n=1}^N n(BA_n) \quad (24)$$

and the total analytical concentration of the central metal, B , may be expressed by

$$B = b + \sum_{n=1}^N (BA_n) \quad (25)$$

where a and b are the concentrations of uncombined ligand and metal and N is the coefficient of the highest BA_n complex.

In most studies B and A are known.

Other frequently employed functions are the average ligand number or Bjerrum's \bar{n} ,

$$\bar{n} = \frac{A-a}{B} = \frac{\sum_{n=1}^N n(BA_n)}{b + \sum_{n=1}^N (BA_n)} = \frac{\sum_{n=1}^N n\beta_n a^n}{1 + \sum_{n=1}^N \beta_n a^n} \quad (26)$$

and the degree of formation, α_n , of the BA_n complex,

$$\alpha_n = \frac{(BA_n)}{B} = \frac{\beta_n a^n}{\sum_{n=1}^N \beta_n a^n} \quad (27)$$

Both Leden's and Fronaeus' computational methods employ the function, F ,

$$F = \beta_1 + \beta_2 a + \beta_3 a^2 + \dots = \sum_{n=1}^N \beta_n a^{n-1} \quad (28)$$

A value for β_1 is determined by extrapolating a plot of F as a function of a to $a = 0$. A value for β_2 is determined from a second function, G ,

$$G = \frac{F - \beta_1}{a} = \beta_2 + \beta_3 a + \dots = \sum_{n=1}^N \beta_n a^{n-2} \quad (29)$$

by extrapolating a plot of G vs. a to $a = 0$. The higher β_n values are determined in an analogous manner.

In Leden's method F is calculated from

$$F = \frac{B-b}{b a} \quad (30)$$

Hence, the concentrations of both the uncombined metal, b , and the uncombined ligand, a , must be determined experiment-

ally or must be readily calculable from experimental measurements.

In the method of Fronaeus the function, F , is determined from

$$\ln F = \int_0^a \frac{\bar{n}}{a} da \quad (31)$$

by graphical integration.

Other computational methods may be employed which use \bar{n} as the starting function. Since B and A are usually known, a value of \bar{n} for each experimental data point may be calculated from an experimental measurement of a . Mathematically all that is necessary is to obtain N experimental points giving N equations of \bar{n} which may be rearranged to the form,

$$\sum_{n=0}^N (\bar{n} - n) \beta_n a^n = 0 \quad (32)$$

which may be solved by determinates using Cramer's rule.

The data points are generally selected at half-integral values of \bar{n} . At these values of \bar{n} the concentrations of the BA_{n-1} and BA_n complexes are approximately equal. This method is not recommended for the most accurate work since a limited amount of experimental data is used.

Several other graphical techniques treating \bar{n} and a data are described in Rossotti and Rossotti (49). These like the graphical techniques of Leden and Fronaeus have common disadvantages. They frequently are lacking objectivity. In the extrapolation procedure the few data points near the extrapo-

lation limit are often weighted more heavily than the other points. Also, due to the nature of the computation, errors tend to accumulate in the higher β_n values.

With the advent of high speed computers more objective and more accurate computational techniques may be used. All the experimental data can be treated simultaneously and other useful parameters may often be obtained from the computations. For example, in the least squares method to be described in the next section the output of the computer program includes a value of the estimated standard deviation of each of the values of β_n .

C. The Weighted Least Squares Computer Program

The weighted least squares computer program was written by Stagg and Powell (55) for an IBM 7074 computer. The program was patterned after a similar program by Sullivan et al. (58).

The \bar{n} expression, Equation 26, can readily be rearranged to the form,

$$\bar{n} = \sum_{n=0}^N \beta_n a^n (A-a-nB) = 0 . \quad (33)$$

In a typical least squares manner this above expression is set equal to a residual, U_1 ,

$$U_1 = \sum_{n=0}^N \beta_n a^n (A-a-nB) \quad (34)$$

and a value of U_1 is calculated for each datum point.

Because of experimental error in the measurement of a , these residual values are seldom equal to zero. Further, the experimental system is one which is ill-conditioned in that the independent variable, a , must be varied over several orders of magnitude while the dependent variable, \bar{n} , changes by a relatively small amount. From the computational viewpoint this ill-conditioning means that there are a large number of nearly correct solutions of the equations which leads to some difficulty in obtaining numerical values for the parameters.

The program then calculates the weighted sum of squares, S , of these residuals,

$$S = \sum_{i=1}^I w_1 U_1^2 \quad (35)$$

where I is the total number of datum points. The weighting factor, w_1 , is arbitrary but the one most frequently used in this type of calculation and the one used in this specific program is

$$w_1 = \frac{1}{\delta U_1^2} \quad (36)$$

where δU_1 is assumed to be due principally to error in the experimental measurement of a ,

$$\delta U_1 = \frac{\partial U_1}{\partial a_1} aH \quad (37)$$

and H is the relative error in the determination of a .

The weighted sum of squares is then minimized with respect to each of the β_n 's

$$\frac{\partial S}{\partial \beta_n} = 0 \quad (38)$$

which results in N equations which are functions of the β_n 's. The individual values of β_n are computed from these N equations by using Cramer's rule.

The estimated standard deviation, σ_n of each of the β_n 's is obtained from the diagonal elements of the inverse matrix of the coefficients of the β_n 's.

$$\sigma_n = \pm \left[\frac{r_{nn}S}{I-N} \right]^{\frac{1}{2}} \quad (39)$$

where r_{nn} is the diagonal element of the inverse coefficient matrix.

The program employs an iterative technique wherein the estimated values of the β_n 's are used to compute U_1 and w_1 . Using these the sum S is calculated and it is then minimized giving new, better values for the β_n 's. The iteration continues until the values of β_n converge to an acceptable limit, which in this specific program is agreement to within 0.001. Generally about six iterations were necessary.

The program input includes values for A, B and a for each experimental datum point and estimations for each β_n . The output includes the calculated values for each β_n with its value for σ_n and two \bar{n} values, an experimental \bar{n} and a calculated \bar{n} , for each datum point. The experimental \bar{n} is obtained from

$$\bar{n} = \frac{A - a}{B} \quad (40)$$

and the calculated \bar{n} is obtained from

$$\bar{n} = \frac{\sum_{n=1}^N n \beta_n a^n}{\sum_{n=1}^N \beta_n a^n} \quad (41)$$

using the calculated values for the β_n 's. The agreement between the two values of \bar{n} is a measure of the quality of the computer program's fit to the experimental data.

IV. APPARATUS AND REAGENTS

The potentiometric measurements were made with a Leeds and Northrup No. 7552 Type K-2 potentiometer coupled with a No. 2430-C Type E galvanometer having a sensitivity of 0.005 μ amp/mm. Titrations were conducted in a constant temperature bath at $25^{\circ} \pm 0.005^{\circ}\text{C}$.

All reagents used were of reagent-grade quality except the potassium nitrate which was a primary standard grade. The 1,10-phenanthroline used was purchased from Aldrich Chemical Company and its purity was checked by nonaqueous acid-base titration in acetonitrile using standardized perchloric acid as the titrant. Stock solutions of zinc sulfate and cadmium sulfate were standardized by titration with standardized ethylenediaminetetraacetic acid.

The deionized water which was used to prepare the unbuffered basic solutions was boiled to drive off carbon dioxide. The water was stored in and delivered from a dispensing bottle which was protected from atmospheric carbon dioxide by a gas-drying tube filled with Ascarite.

The conditional over-all formation constants were calculated on an IBM 7074 computer.

V. EXPERIMENTAL PROCEDURES AND RESULTS

A. Introduction

The Ag/AgP₂NO₃ electrode was devised by Grimes (24) to determine the concentration of uncombined 1,10-phenanthroline. Its utility in studying metal-1,10-phenanthroline systems was pursued by Fullerton (20). Grimes (24) cited the work of Schmid and Reilley (52) and Schwarzenbach and Anderegg (53) as the inspiration for the development of the electrode.

Schmid and Reilley (52) have employed a mercury electrode in the determination of the values of β_1 of the chelates of ethylenediaminetetraacetic acid (Z) with several metals. The method is based upon the competition between the metal being studied, M, and mercury(II) for Z,



where z is the ionic charge of M.

The potential of the mercury electrode is indicative of the concentration of uncombined mercury(II). A combination of the Nernst equation for the mercury electrode at 25°C with the equations for the formation constants of the mercury and metal chelates gives

$$E = E^{\circ}_{\text{Hg}^{+2}/\text{Hg}} + 0.0296 \log \frac{(\text{M})(\text{HgZ})}{(\text{MZ})\beta_{\text{HgZ}}} + 0.0296 \log \beta_{\text{MZ}} \quad (43)$$

Hence the potential of the mercury electrode depends linearly on $\log \beta_{\text{MZ}}$ if the concentrations of HgZ, MZ, and M remain constant. The values of β_{MZ} were calculated directly from the experimental data and the previously determined

value for β_{HgZ} .

The authors suggest that the method is rapid and simple for 1:1 metal chelates but it would be considerably more complex in the study of metal-ligand systems which involve higher order complexes.

Schwarzenbach and Anderegg (53) have determined the values of β_{MZ} for some MZ chelates by a potentiometric technique employing mercury(II) as the competing ion. Solutions containing known quantities of the HgZ and MZ chelates were prepared. The equilibrium concentration of uncomplexed mercury(II) was determined potentiometrically with a mercury electrode. The concentration of uncombined Z in the system could then be calculated from the previously determined value for β_{HgZ} . The value for β_{MZ} may then be obtained from the total concentrations of the metal and Z and the value for the concentration of uncombined Z.

Dale (13) used a similar potentiometric technique with silver(I) as the competing ion to determine the values of β_n for the stepwise chelates of 1,10-phenanthroline with some transition metals. By a titration technique the total concentration of 1,10-phenanthroline was varied while the total concentrations of silver and the metal being studied were held constant. In the system the concentration of uncombined silver(I) was determined potentiometrically with a silver electrode. The concentration of uncombined 1,10-phenanthroline could then be determined from the previously determined

values of β_n for the AgP_1^{+1} and AgP_2^{+1} complexes and the measured concentration of uncombined silver(I). Using the values for the total concentrations of metal and ligand and the calculated value for uncombined ligand, the values of \bar{n} for each experimental datum point could be obtained. The values of β_n for the MP_n^{+z} complexes were calculated by a weighted least squares computer program.

Anderegg (1) employed a similar competitive, potentiometric technique to study metal-1,10-phenanthroline systems. Mercury(II) was the competing ion and a mercury electrode was used to determine the concentration of uncombined mercury(II). A precipitate of $\text{Hg}_2\text{P}_2(\text{NO}_3)_2$ formed in the system giving, essentially, a second order electrode, $\text{Hg}/\text{Hg}_2\text{P}_2(\text{NO}_3)_2$.

By far the most commonly used competitive technique involves the use of the hydrogen(I) as the competing ion. The literature is replete with the use of the glass electrode to determine the values of β_n for a metal-ligand system. The concentration of uncombined ligand is determined from the experimentally determined pH and the previously determined formation constant(s) of the hydrogen-ligand species. Rossotti and Rossotti (49) have reviewed the various ramifications of this technique.

Grimes (24) did some preliminary investigation into the utility of the mercury electrode for the study of metal-1,10-phenanthroline systems. However this approach was discarded

because the preliminary investigation indicated that the reaction between mercury(II) and 1,10-phenanthroline was very complex.

Grimes (24) and later Fullerton (20) studied the reaction between silver(I) and 1,10-phenanthroline. Grimes (24) titrated a 2.5×10^{-3} M AgNO_3 solution with 1.1×10^{-2} M 1,10-phenanthroline. The course of the titration was followed with a silver-saturated calomel electrode pair. A 0.1 M KNO_3 agar-agar salt bridge was used. No mention was made of controlling the ionic strength. A light yellow precipitate formed after the addition of a few drops of 1,10-phenanthroline solution. A large potential break of about 250 to 300 millivolts was observed in the plot of electrode potential vs. moles of 1,10-phenanthroline added per mole of AgNO_3 . The position of the potential break indicated the formation of bis(1,10-phenanthroline)silver(I).

No indication of the formation of a tris(1,10-phenanthroline)silver(I) or a mono(1,10-phenanthroline)silver(I) complex was observed. This indicates that the second step formation constant is quite large and that the tris complex is weak or nonexistent.

To characterize the precipitate which formed in the titration Grimes (24) dissolved a quantity of the precipitate in 0.1 M H_2SO_4 and determined the amount of 1,10-phenanthroline by ultraviolet spectrophotometry. The result indicated

that the precipitate was bis(1,10-phenanthroline)silver(I) nitrate, AgP_2NO_3 .

A similar titration of silver sulfate with 1,10-phenanthroline was performed. The character of potentiometric plot was identical to that obtained in the prior titration. One principal difference was noted. No precipitate formed in this titration.

Because the insolubility of AgP_2NO_3 would simplify the use of the competitive method in the study of metal-1,10-phenanthroline systems, Grimes (24) chose to further develop and utilize the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode.

The values of β_2 for the AgP_2^{+1} chelate and the solubility product constant, K_{sp} , for AgP_2NO_3 were determined from the above titrations. Grimes (24) reported values of $10^{11.6}$ and $10^{-8.8}$ respectively, while Fullerton (20) reported values of $10^{11.42}$ and $10^{-8.49}$. The mode of calculation used by Fullerton (20) involves the following equations:

$$\beta_2 = \frac{(\text{AgP}_2^{+1})}{(\text{Ag}^{+1})(\text{P})^2} \quad (44)$$

$$(\text{P}_\text{T}) = (\text{P}) + (\text{HP}^{+1}) + 2(\text{AgP}_2^{+1}) \quad (45)$$

$$(\text{Ag}^{+1}_\text{T}) = (\text{Ag}^{+1}) + (\text{AgP}_2^{+1}) . \quad (46)$$

Experimental points from the above described titrations were used. The points were taken after the equivalence point of the titration so that the AgP_1^{+1} species could be ignored

in the computations. Equations 44, 45 and 46 are then combined to give

$$\beta_2 = \frac{(\text{Ag}_T^{+1}) - (\text{Ag}^{+1})}{(\text{Ag}^{+1}) \left[\frac{(\text{P}_T) - 2(\text{Ag}^{+1}_T) - 2(\text{Ag}^{+1})}{1 + \beta_{1\text{HP}} (\text{H}^{+1})} \right]^2} \quad (47)$$

The value of β_2 was then determined from the experimentally measured pH and concentration of uncombined silver(I) in a solution of known total concentrations of silver and 1,10-phenanthroline.

Similarly the K_{sp} for AgP_2NO_3 ,

$$K_{\text{sp}} = (\text{AgP}_2^{+1})(\text{NO}_3^{-1}) \quad (48)$$

was determined assuming that after the equivalence point in the titration

$$(\text{NO}_3^{-1}) = (\text{AgP}_2^{+1}) + (\text{Ag}^{+1}) \cong (\text{AgP}_2^{+1}). \quad (49)$$

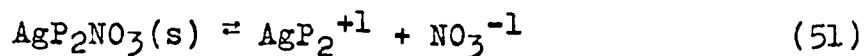
The final expression used by Fullerton (20) was

$$K_{\text{sp}} = \left[\beta_2 (\text{Ag}^{+1}) \left[\frac{(\text{P}_T) - 2(\text{Ag}^{+1}_T) + 2(\text{Ag}^{+1})}{1 + \beta_{1\text{HP}} (\text{H}^{+1})} \right] \right]^2 \quad (50)$$

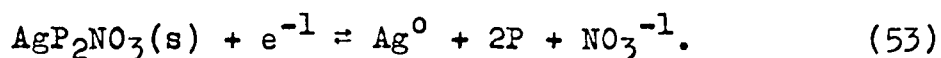
B. The $\text{Ag}/\text{AgP}_2\text{NO}_3$ Electrode

In the present work the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode was used to determine the concentration of uncombined 1,10-phenanthroline. The electrode is an electrode of the second kind analogous to the silver halide, Ag/AgX , electrodes. That is, it consists of a metal, silver, and an insoluble salt of the metal,

AgP_2NO_3 . The electrode reaction is somewhat more involved than the Ag/AgX electrode reaction in that the complex cation, AgP_2^{+1} , has a dissociation reaction which must be considered



The overall electrode reaction is



Upon considering Equations 44 and 48 it can be shown that the concentration of uncombined silver(I) in a solution saturated in AgP_2NO_3 is

$$(\text{Ag}^{+1}) = \frac{K_{\text{sp}}}{\beta_2(\text{P})^2(\text{NO}_3^{-1})}. \quad (54)$$

A silver electrode dipping into a solution saturated in AgP_2NO_3 would respond to this concentration of uncombined silver(I) according to the Nernst equation at 25°C ,

$$E = E^\circ_{\text{Ag}^{+1}/\text{Ag}} + 0.059 \log (\text{Ag}^{+1}) \quad (55)$$

$$\begin{aligned} &= E^\circ_{\text{Ag}^{+1}/\text{Ag}} + 0.059 \log \frac{K_{\text{sp}}}{\beta_2} - 0.059 \log(\text{NO}_3^{-1}) \\ &\quad - 0.118 \log(\text{P}). \end{aligned} \quad (56)$$

The potential of the silver electrode then is dependent upon the concentrations of nitrate ion and uncombined 1,10-phenanthroline. If the concentration of nitrate ion is kept constant or if the electrode potential is corrected for the

nitrate ion contribution, the potential of the silver electrode will be dependent only upon the concentration of uncombined 1,10-phenanthroline.

The first two terms in Equation 56 are essentially the E° for the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode, $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$,

$$E = E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3} - 0.059 \log(\text{NO}_3^{-1}) - 0.118 \log(P). \quad (57)$$

A value for $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$ was calculated by Fullerton (20) from these terms. The value obtained was -0.378 volt vs. the SCE. Grimes (24) experimentally determined $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$. He performed a titration of a solution containing $1 \times 10^{-4} \text{ M}$ KOH, $1 \times 10^{-4} \text{ M}$ KNO_3 and $1 \times 10^{-2} \text{ M}$ 1,10-phenanthroline with a titrant solution containing $1 \times 10^{-4} \text{ M}$ KOH and $1 \times 10^{-4} \text{ M}$ KNO_3 . The concentration of 1,10-phenanthroline was varied from $1 \times 10^{-2} \text{ M}$ to $5 \times 10^{-3} \text{ M}$. The course of the titration was followed with a $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode. A saturated calomel electrode, separated from the titration solution by a 0.1 M KNO_3 agar-agar salt bridge, was used as the reference electrode. Equation 57 was used to calculate the value for $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$. A value of -0.311 volt vs. the SCE was obtained.

Grimes (24) and Fullerton (20) used the electrode in a direct potentiometric technique. That is, they calculated concentrations of uncombined 1,10-phenanthroline from the experimentally measured electrode potentials using Equation

57. Corrections for the nitrate ion contribution to the electrode potential had to be made. As previously noted the $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$ used by Fullerton (20) was calculated from Equation 56 which includes the value of β_2 for AgP_2^{+1} and the K_{sp} value for AgP_2NO_3 . These values were in turn determined from the titrations where the ionic strength was not controlled. Hence, the exact validity of his $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$ in the hydrogen- and metal-1,10-phenanthroline systems is questionable.

The same criticism applies to the work by Grimes (24). The $E^{\circ}_{\text{Ag}/\text{AgP}_2\text{NO}_3}$ was determined at an ionic strength of about $2 \times 10^{-4} \text{ M}$ while the ionic strength in his hydrogen-1,10-phenanthroline study was about 0.07.

When one employs direct potentiometry the results are only as good as the ability to reproducibly prepare the electrodes. Further, for the best results one must eliminate or render constant any undesirable effects due to liquid junction potentials.

C. Electrode Preparation

The procedure used to prepare the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes was similar to that described by Meites and Thomas (43) for Ag/AgCl electrodes. Silver electrodes were cleaned by dipping them into 6 M HNO_3 for about one minute. After rinsing thoroughly with distilled water, the electrodes were anodically oxidized for two minutes in a solution which contained

$1 \times 10^{-3} \text{ M KNO}_3$ and $1 \times 10^{-2} \text{ M 1,10-phenanthroline}$. A 1.5-volt dry cell was used as the source of current and a circular platinum gauze electrode was used as the auxiliary electrode. The current density was about 0.5 mamp/cm^2 .

Two types of silver electrodes were used. Some were commercial silver billet electrodes (Beckman 39261) while the others were prepared in this laboratory from 20 gauge silver wire. The end of the silver wire was wrapped into a helix. The wire was then heat sealed into a length of soft glass tubing leaving only the helical portion of the wire exposed to the solution.

The electrodes were anodically oxidized before each titration. The titration medium was kept saturated in AgP_2NO_3 by an addition of an excess of the insoluble salt to the solutions being used.

Five $\text{Ag/AgP}_2\text{NO}_3$ electrodes (two silver billet electrodes and three silver wire electrodes) were employed in the titration used to prepare the standard $\text{Ag/AgP}_2\text{NO}_3$ electrode response plot and in the titrations in the metal- and hydrogen-1,10-phenanthroline studies. An average value for the concentration of uncombined 1,10-phenanthroline in the metal- and hydrogen-1,10-phenanthroline studies was calculated from the values indicated by the five electrodes. This average value was used in the computation of the over-all formation constants.

Grimes (24) and Fullerton (20) prepared their $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes in a somewhat different manner. Silver billet electrodes were cleaned and polished with scouring powder and the electrodes were electroplated for about 45 minutes to produce a much thicker layer of AgP_2NO_3 . This author and Dale (14) experienced difficulty in preparing reproducible electrodes by this procedure.

D. Summary of the Potentiometric Procedure Used to
Obtain the Over-all Formation Constants

To minimize the problems cited in the direct potentiometric technique employed by Grimes (24) and Fullerton (20) the following procedure was used. By a titration procedure the concentration of uncombined 1,10-phenanthroline was varied from about $3 \times 10^{-5} \text{ M}$ to about $1 \times 10^{-2} \text{ M}$ while the concentrations of KOH and KNO_3 were kept constant at $1 \times 10^{-4} \text{ M}$. The ionic strength was maintained at 0.1 with K_2SO_4 . The solution was saturated in AgP_2NO_3 by the addition of an excess of the solid salt. Anodically oxidized silver electrodes were placed in the solution and their potential vs. the SCE was measured as the titration was performed. A standard $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode plot of electrode potential vs. the $\log(P)$ was prepared.

A second titration was performed in an identical manner to the above titration except that the solution contained $5.105 \times 10^{-3} \text{ M}$ H_2SO_4 instead of the KOH . From the electrode

potentials obtained in this latter titration and the standard electrode response plot obtained in the former titration, values of the concentration of uncombined 1,10-phenanthroline for each experimental datum point can be determined. In this manner the experimental data necessary to compute the formation constants of the HP_n^{+1} species was obtained.

E. Apparatus Used in the Potentiometric Investigation

The titrations were conducted in a stoppered Teflon beaker (400 ml.). The titration system was continually flushed with carbon dioxide-free helium to minimize adsorption of atmospheric carbon dioxide by the unbuffered basic solution used in procedure for the preparation of the standard Ag/AgP_2NO_3 electrode response plot. The titrant solution in the buret was protected from atmospheric carbon dioxide by a drying tube containing Ascarite.

A fiber type saturated calomel electrode was used as the reference electrode. It was placed in a beaker containing 0.0333 M K_2SO_4 ($\mu = 0.1$). The reference electrode compartment was connected to the titration system by a salt bridge employing ultrafine porosity Pyrex disks to minimize solution transfer. Several salt bridge solutions were considered. These solutions were evaluated by considering their compatibility with the titration solution and from their effect on the junction potential of the system.

The salt bridge solution is essentially limited to a sulfate salt. Nitrate salts are unfavorable since the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode responds to nitrate ion. Seepage of chloride ion into the titration vessel would be unfavorable because of the effect the chloride ion would have on the electrode system. Perchlorate salts are unfavorable since many metal-1,10-phenanthroline perchlorate salts are insoluble.

To estimate the magnitude of the junction potential, E_j , between two solutions at 25°C the well known Henderson equation which may be found in most advanced texts on electrochemistry (39) was used

$$E_j = \frac{0.059}{n} \frac{\sum_{i=1}^I U_i/z_i (C_i'' - C_i')}{\sum_{i=1}^I U_i (C_i'' - C_i')} \log \frac{\sum_{i=1}^I C_i' U_i}{\sum_{i=1}^I C_i'' U_i} \quad (58)$$

where U_i is the mobility of an ion of charge, z_i , and C' and C'' are the concentrations of the ion on the right and left hand side of the junction respectively. In most work materials like potassium chloride or potassium nitrate are used in high concentration in the salt bridge to minimize the potential at the liquid junctions. The mobilities of the anion and cation of these salts are nearly equal. However, for reasons mentioned above these materials are unfavorable in this system.

With potassium sulfate as the salt bridge solution the

estimated junction potentials are generally larger but they can be rendered negligible by having nearly identical solutions on each side of the junction. For this reason a 0.0333 M K_2SO_4 solution similar to that used in the titration solutions was employed as the salt bridge solution in all the titrations.

F. The Reaction Between Potassium Ion and 1,10-Phenanthroline

The assumption inherent in the preparation of the standard response plot is that when the concentration of 1,10-phenanthroline is altered by the addition of the titrant, there is no combination of 1,10-phenanthroline taking place. That is, all the added 1,10-phenanthroline is free or uncombined.

However, the titration medium, as previously noted, contains a considerable amount of potassium ion and Grimes (24) and Fullerton (20) report that 1,10-phenanthroline reacts with the alkali metals. They determined values of the β_n 's for the 1:1 and 1:2 1,10-phenanthroline complexes of lithium, sodium and potassium. Their reported values for the $\log \beta_n$ of the KP_1^{+1} and KP_2^{+1} complexes were 2.09 and 4.93 (24) and 1.0 and 5.09 (20).

Dale (14) felt that these values were excessive and he concluded that complexation of potassium ion by 1,10-phenanthroline was negligible in his study. The evidence cited included no significant change in the potential value of a

silver electrode dipping into a solution of silver ion, 1,10-phenanthroline and a variable concentration of potassium sulfate. Further, Dale (14) cited that there was no noticeable decrease of the ultraviolet absorption peaks of a 1,10-phenanthroline solution even in 1 M KCl.

If the complexation of potassium ion by 1,10-phenanthroline was significant, an electrode potential measurement with a glass electrode responsive to univalent cations, having the following response at 25°C,

$$E = \text{constant} - 0.059 \log (K^{+1})$$

could be used to detect a change in the concentration of uncomplexed potassium ion. Two solutions each containing 5×10^{-4} M K_2SO_4 and 1×10^{-4} M KOH were prepared. One solution also contained 1×10^{-2} M 1,10-phenanthroline. If there is complexation of potassium ion by 1,10-phenanthroline, the total concentration of potassium ion, K_T^{+1} , would be

$$(K_T^{+1}) = (K^{+1}) + (KP_1^{+1}) + (KP_2^{+1}) \quad (59)$$

$$= (K^{+1}) [1 + \beta_1(P) + \beta_2(P)^2] \quad (60)$$

Hence, the concentration of uncomplexed potassium ion would be lower in the solution containing 1,10-phenanthroline. Using the values of β_n reported by Grimes (24) and Fullerton (20) a minimum electrode potential difference of about fifty millivolts should be observed between the two solutions. Duplicate electrode potential values vs. a SCE were obtained on the two solutions. The results on the solution which contained 1,10-

phenanthroline were 113 and 112 millivolts, and the results on the solution which did not contain 1,10-phenanthroline were 112 and 112 millivolts.

These results indicate that there is no significant complexation of potassium by 1,10-phenanthroline under these experimental conditions. This is another piece of evidence indicating that the values of β_n reported by Grimes (24) and Fullerton (20) for the KP_1^{+1} and KP_2^{+1} species are indeed excessive.

The solubility study to be described below further indicates that no complexation of potassium occurs even in solutions saturated in 1,10-phenanthroline.

As a result of these studies it was decided that the interaction between potassium ion and 1,10-phenanthroline was negligible in the present investigation.

G. The Standard Ag/AgP_2NO_3 Electrode Response Plot

The electrode response plot was obtained in the following manner. Two solutions were prepared. The solutions were of identical composition except that one solution, the titrant, contained a known concentration of 1,10-phenanthroline, about 0.015 M. Both solutions contained 1.000×10^{-4} M KNO_3 to maintain a constant nitrate ion concentration. Hence, the contribution by nitrate ion to the potential of the Ag/AgP_2NO_3 electrode would be constant throughout the titration. Both solutions contained 1×10^{-4} M KOH to keep the pH

of the medium at 10 to inhibit the reaction between hydrogen ion and 1,10-phenanthroline. In this manner all the added 1,10-phenanthroline would be uncombined. Both solutions contained potassium sulfate to maintain the ionic strength at 0.1. At constant ionic strength the activity coefficients remain constant so that concentrations instead of activities of the ionic components in the system could be employed in the subsequent calculations.

Forty milliliters of the solution which had no 1,10-phenanthroline was then titrated with the titrant solution which contained 1,10-phenanthroline. By this procedure the concentration of 1,10-phenanthroline in the system was varied over about two orders of magnitude while the nitrate ion concentration, pH and ionic strength of the medium were held constant.

The system was usually quite slow in coming to steady potential values particularly when the concentration of 1,10-phenanthroline was low. This was undoubtedly due to the complex nature of the electrode reaction. It was often necessary to allow the system to equilibrate for more than an hour from the time of the addition of the titrant to when reasonably steady electrode potentials were obtained. Potential readings were taken every five minutes and the system was considered to be at equilibrium when successive electrode potential values varied by less than about 0.15 millivolt.

A standard electrode response plot of $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode potential vs. the concentration of uncombined 1,10-phenanthroline was prepared for each of the five $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes. The standard electrode response plot of a typical $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode is shown in Figure 1.

The response plots for the electrodes consisted of two regions both of which were in themselves colinear, but the two regions had slightly different, non-Nernstian slopes. The inflection point occurred at about $2 \times 10^{-3} \text{ M}$ 1,10-phenanthroline. The slope of the region of low concentration of 1,10-phenanthroline was always greater than the slope of the high 1,10-phenanthroline region. Two experimental trials consisting of two titrations each were used to prepare the standard electrode response plots for the investigation of the HP_n^{+1} system. The slope values for the individual $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes in each trial are listed in Table 1.

Table 1. Experimental slope values of the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes in the standard electrode response plot^a

Electrode	Slope	
	Trial 1	Trial 2
Silver billet 1	96/94	97/95
Silver billet 2	102/93	102/93
Silver wire 4	108/98	110/95
Silver wire 5	109/98	112/92
Silver wire 6	108/97	111/98

^aValues obtained at $1.000 \times 10^{-4} \text{ M}$ KNO_3 , $\text{pH} = 10$, $\mu = 0.1$ and $t = 25^\circ \pm 0.05^\circ\text{C}$.

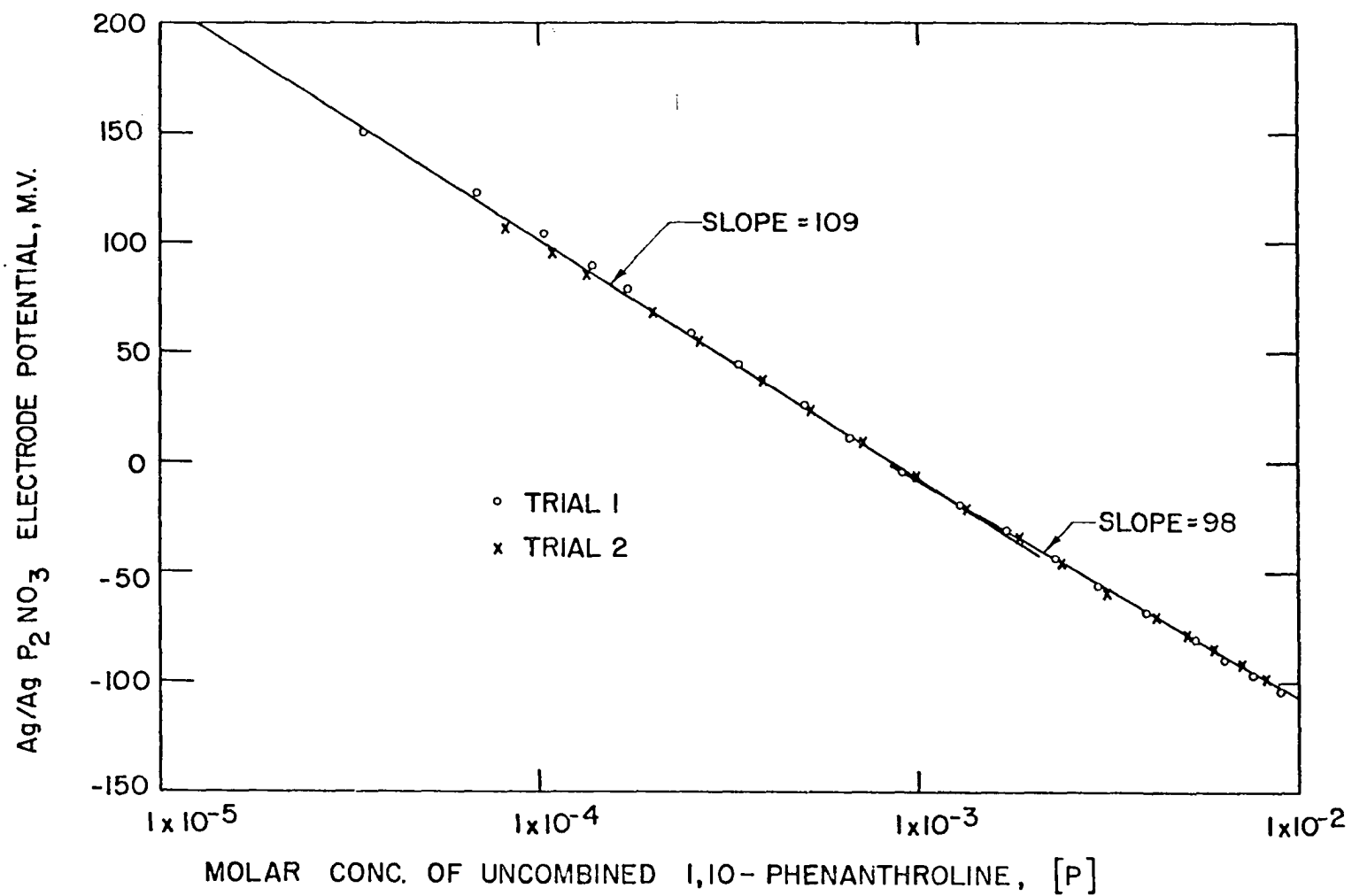


Figure 1. Standard Ag/AgP₂NO₃ electrode response plot

The slope values are listed in the following manner: slope of the region of low concentration of 1,10-phenanthroline/ slope of the region of high concentration of 1,10-phenanthroline. The theoretical Nernstian value for the slope is 118.30 millivolts.

This type of non-Nernstian, two-slope response was observed with both the silver billet and silver wire electrodes. It was observed in titrations carried out at low ionic strength (2×10^{-4}) as well as in the titrations at an ionic strength of 0.1. The difference in slope values of the two regions was greater at the lower ionic strength. Slope values of about 105/80 were observed with the silver billet electrodes and values of about 113/83 were observed with the silver wire electrodes at the lower ionic strength. Similar electrode response plots were also obtained in a system where tetramethylammonium sulfate instead of potassium sulfate was used to control the ionic strength. The two-slope electrode response plots were observed when titrations were conducted at higher concentrations of potassium nitrate. Similar results were observed when different materials were used in the salt bridge and also when the titration solutions were or were not presaturated by the addition of excess, solid AgP_2NO_3 . Some $\text{Ag}/\text{AgP}_2\text{ClO}_4$ electrodes were prepared. They behaved like the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrodes in their response to the concentrations of uncombined 1,10-phenanthroline. Some Ag/AgCl electrodes were prepared and their response to the

concentration of chloride ion at an ionic strength of 0.1 (KNO_3) was determined. The Ag/AgCl electrode response plot was linear from 1×10^{-4} to 1×10^{-2} M KCl with a slope value of about 54.5 compared to the theoretical Nernstian value of 59.15.

This type of two-slope, non-Nernstian response has been reported by other workers. Bishop and Dhaneshwar (9) have observed a two-slope, non-Nernstian response of various types of silver and silver halide electrodes to the concentrations of both silver and halide ions. They report that the electrodes respond to the concentration of silver ion with an efficiency of 65 to 75 per cent which results in slope values differing from the theoretical value. They also suggest that this behavior is not well documented since most workers are concerned with the performance of the silver halide electrodes as reference electrodes and not with their performance as indicator electrodes.

H. The Over-all Formation Constants for the Hydrogen-1,10-phenanthroline Species

In the determination of the values of β_n for the HP_n^{+1} species a titration was conducted in a similar manner to that used to obtain the standard $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode response plots except that the two solutions used in the titration contained 5.105×10^{-3} M H_2SO_4 in place of 1×10^{-4} M KOH . Both solutions contained 1.000×10^{-4} M KNO_3 and had an ionic

strength of 0.1 (K_2SO_4). Three experimental trials were conducted. The titrant solutions contained about $3.7 \times 10^{-2} M$ 1,10-phenanthroline. The concentration of uncombined 1,10-phenanthroline at each datum point was determined for each of the Ag/AgP_2NO_3 electrodes using the electrode potential values in the HP_n^{+1} titration and the previously obtained standard Ag/AgP_2NO_3 electrode response plot for each electrode.

The plot of Ag/AgP_2NO_3 electrode potential, \bar{E} , vs. $\log (P_T)$ for a HP_n^{+1} titration is shown in Figure 2. Tables 2-4 show the progress of the titrations for each HP_n^{+1} experimental trial. The values reported for the Ag/AgP_2NO_3 electrode potential, \bar{E} , and for the concentration of uncombined 1,10-phenanthroline, \bar{P} , are average values from the five Ag/AgP_2NO_3 electrodes. The experimental \bar{n} values, \bar{n}_e , are calculated from Equation 40 and the calculated \bar{n} values, \bar{n}_c , are calculated in the computer program from Equation 41 using the previously determined conditional over-all formation constants of the HP_n^{+1} species. The agreement between the two values for \bar{n} is a measure of the fit of the weighted least squares computer program to the experimental data. The formation curve of \bar{n} vs. $\log (P)$ is a graphical representation of this fit. Figure 3 shows the formation curve for Trial 1 of the HP_n^{+1} study. Figure 10 which is shown later compares the formation curve of the HP_n^{+1} system with those obtained in the CdP_n^{+2} and ZnP_n^{+2} studies.

Table 2. The titration of hydrogen(I) with 1,10-phenanthroline, trial 1^a

Titrant (ml.)	$P_2 \times 10^2$ (<u>M</u>)	\bar{E} (mv.)	\bar{P} (<u>M</u>)	\bar{n}_e	\bar{n}_c
1.50	0.1263	264.9	2.36×10^{-6}	0.12	0.12
3.00	0.2437	230.4	5.99	0.24	0.25
5.00	0.3881	199.7	1.12×10^{-5}	0.38	0.38
7.00	0.5202	175.7	1.88	0.51	0.51
9.00	0.6416	154.8	2.96	0.63	0.62
11.00	0.7533	132.2	4.86	0.73	0.73
14.00	0.9056	94.0	1.12×10^{-4}	0.88	0.87
17.00	1.042	46.0	3.19	0.99	0.99
20.00	1.164	8.6	6.99	1.07	1.07
24.00	1.310	-20.8	1.34×10^{-3}	1.15	1.16
32.00	1.553	-45.3	2.41	1.29	1.32
45.00	1.849	-63.6	3.51	1.47	1.46
65.00	2.152	-74.7	4.94	1.63	1.63
90.00	2.418	-84.6	6.13	1.77	1.76
140.00	2.717	-93.6	7.62	1.91	1.89
190.00	2.886	-99.1	8.69	1.98	1.98

^aThe titrant solution contained 0.03493 M 1,10-phenanthroline.

Table 3. The titration of hydrogen(I) with 1,10-phenanthroline, trial 2^a

Titrant (ml.)	$P_T \times 10^2$ (<u>M</u>)	\bar{E} (mv.)	\bar{P} (<u>M</u>)	\bar{n}_e	\bar{n}_c
1.50	0.1350	266.4	2.70×10^{-6}	0.13	0.13
3.00	0.2607	229.7	5.89	0.25	0.25
5.00	0.4151	197.9	1.13×10^{-5}	0.41	0.40
7.00	0.5564	173.1	2.03	0.54	0.54
9.00	0.6861	147.8	3.42	0.67	0.67
11.00	0.8059	121.3	6.13	0.78	0.78
14.00	0.9685	72.7	1.76×10^{-4}	0.93	0.93
17.00	1.114	22.0	5.27	1.04	1.04
20.00	1.245	-9.3	1.04×10^{-3}	1.12	1.12
24.00	1.401	-32.4	1.70	1.21	1.21
32.00	1.160	-56.5	2.98	1.33	1.35
45.00	1.973	-74.8	4.65	1.48	1.52
65.00	2.312	-86.4	6.15	1.66	1.65
90.00	2.586	-94.6	7.57	1.79	1.76
140.00	2.906	-103.8	9.57	1.91	1.89

^aThe titrant solution contained 0.03736 M 1,10-phenanthroline.

Table 4. The titration of hydrogen ion with 1,10-phenanthroline, trial 3^a

Titrant (ml.)	$P_T \times 10^2$ (M)	\bar{E} (mv.)	\bar{P} (M)	\bar{n}_e	\bar{n}_c
1.50	0.1355	266.5	2.73×10^{-6}	0.13	0.13
3.00	0.2616	229.8	5.91	0.26	0.25
5.00	0.4166	197.6	1.18×10^{-5}	0.41	0.40
7.00	0.5584	171.5	2.07	0.54	0.54
9.00	0.6836	147.2	3.49	0.67	0.67
11.00	0.8086	120.5	6.23	0.79	0.79
14.00	0.9720	7.10	1.82×10^{-4}	0.93	0.94
17.00	1.118	21.2	9.25	1.04	1.04
20.00	1.250	-10.0	1.05×10^{-3}	1.12	1.12
24.00	1.406	-32.5	1.71	1.21	1.21
32.00	1.667	-56.3	2.98	1.34	1.35
45.00	1.985	-74.2	4.61	1.49	1.51
65.00	2.321	-86.9	6.26	1.66	1.65
90.00	2.592	-95.7	7.72	1.78	1.75
140.00	2.916	-106.3	1.00×10^{-2}	1.88	1.89

^aThe titrant solution contained 0.03749 M 1,10-phenanthroline.

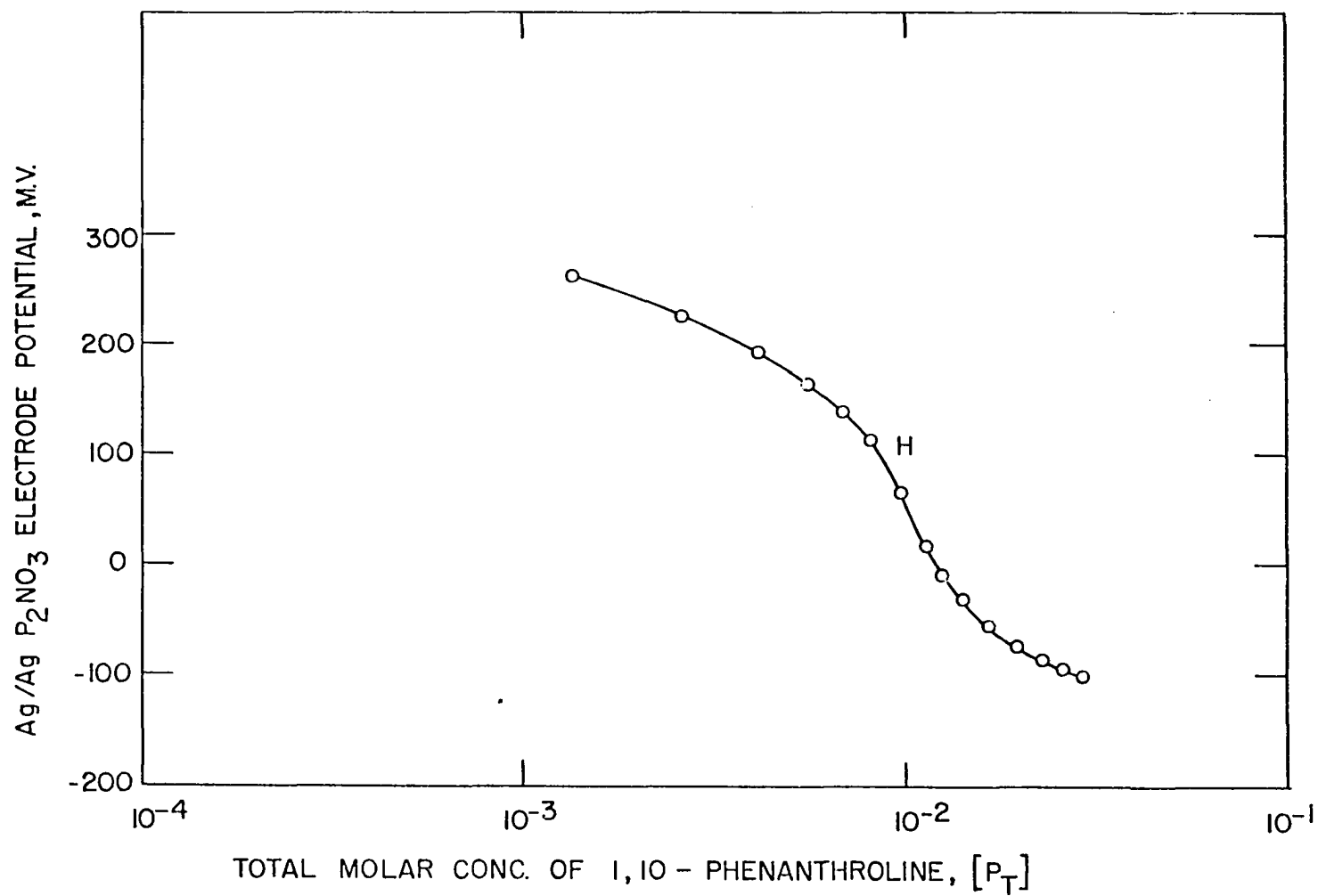


Figure 2. Titration of hydrogen(I) with 1,10-phenanthroline

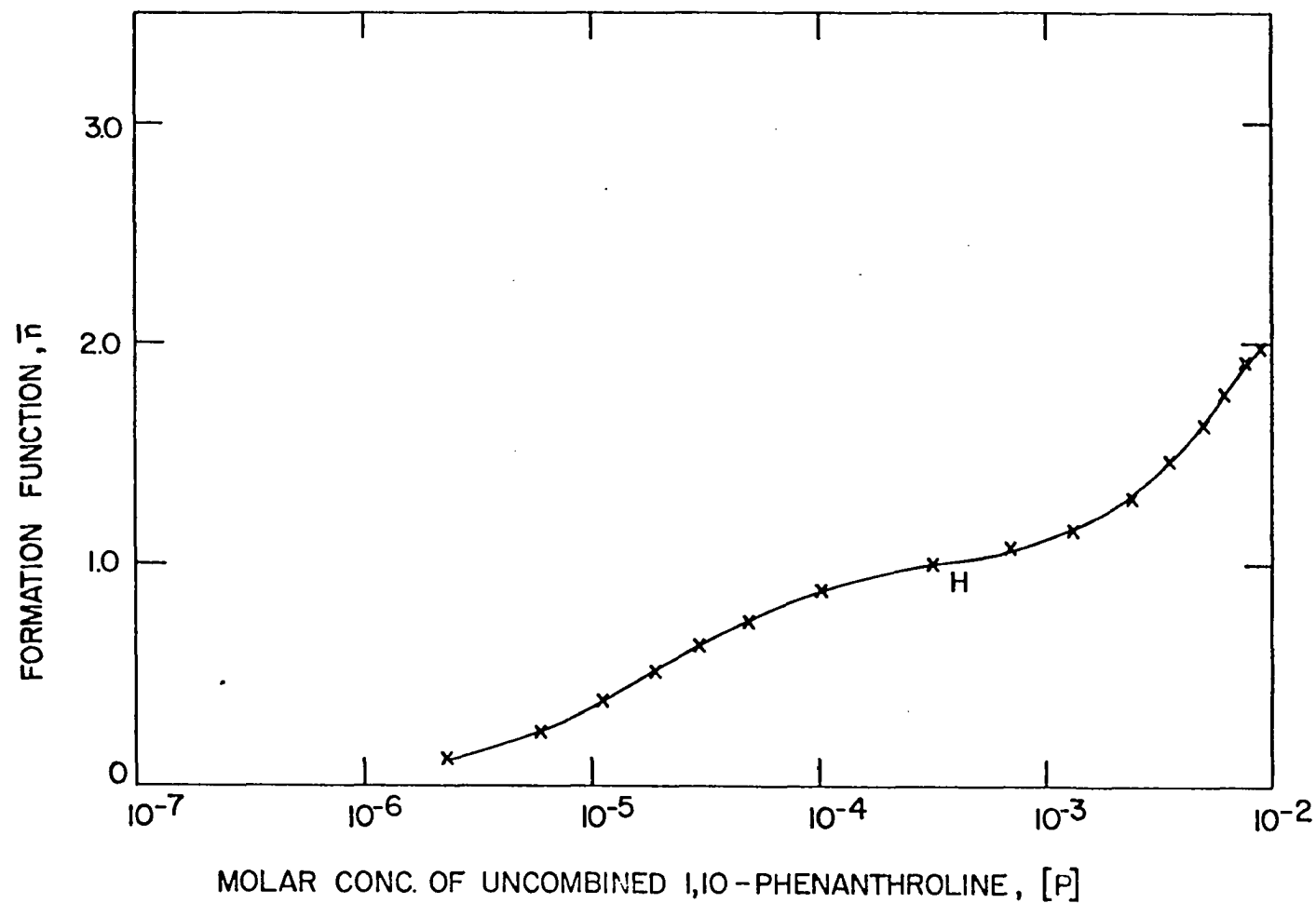


Figure 3. Formation function for hydrogen-1,10-phenanthroline; curve, calculated \bar{n} ; x, experimental \bar{n}

It should be noted that the maximum value of \bar{n} obtained in the potentiometric study was about 1.9. However, a three-parameter least squares computer program, which determines values of β_n for three HP_n^{+1} species, was used for the computations. The principal reason for using a three-parameter program was that the slope of the plot of solubility of 1,10-phenanthroline as a function of the total concentration of hydrochloric acid was 2.23. This is essentially a maximum possible value of \bar{n} for the HP_n^{+1} system which is realized only in solutions saturated in the ligand. A value of \bar{n} greater than two indicates that three species must be considered in the computations. Further, the agreement between the calculated and experimental values of \bar{n} was good for all the experimental data and in the resulting formation curve as the value of \bar{n} approaches two, the curve is still quite steep indicating that values of \bar{n} greater than two would be obtained in higher concentrations of 1,10-phenanthroline.

To further substantiate the validity of the three-parameter program a two-parameter least squares program was tried on the same experimental data. The agreement between the experimental and calculated values of \bar{n} , which is a qualitative measure of the fit of the program to the data, was poor for values of \bar{n} greater than about 1.3. As the value of \bar{n} increased the agreement became poorer, indicating that the system was not adequately described by considering only two

HP_n^{+1} species.

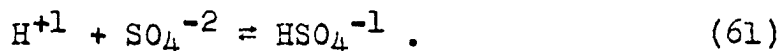
The resulting values of β_n' obtained directly from the computer program are conditional constants which are valid only for the particular set of conditions employed in the experimental system. Table 5 lists the values of $\log \beta_n'$ for the HP_n^{+1} species with their estimated standard deviations.

Table 5. The over-all conditional formation constants for the hydrogen-1,10-phenanthroline species^a

Trial	$\log \beta_1'$	$\log \beta_2'$	$\log \beta_3'$
1	4.76 ± 0.02	6.84 ± 0.07	8.86 ± 0.09
2	4.77 ± 0.01	6.88 ± 0.04	8.66 ± 0.09
3	4.77 ± 0.02	6.90 ± 0.04	8.61 ± 0.10

^aValues are not corrected for the bisulfate ion, $\mu = 0.1$, $t = 25^\circ + 0.05^\circ\text{C}$.

The stoichiometric formation constants, β_n , for the HP_n^{+1} species were obtained by correcting the conditional formation constants for the competing bisulfate reaction



The concentration of hydrogen ion not combined with 1,10-phenanthroline, (H^{+1}) , is

$$(\text{H}^{+1}) = (\text{H}^{+1}) + (\text{HSO}_4^{-1}) \quad (62)$$

$$= (\text{H}^{+1}) [1 + \beta_{\text{HSO}_4}(\text{SO}_4^{-2})] \quad (63)$$

where β_{HSO_4} is the reciprocal of the bisulfate acid dissocia-

tion constant, K_{HSO_4} . An average value of the thermodynamic K_{HSO_4} reported in the literature is 1.02×10^{-2} (28). Using this value and the ionic activity coefficients reported by Kielland (29) a correction factor of 2.25 was obtained. The over-all stoichiometric formation constants for the HP_n^{+1} species are listed in Table 6 with the values reported by other workers.

Table 6. The over-all stoichiometric formation constants of the hydrogen-1,10-phenanthroline species^a

Trial	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Reference
1	5.11	7.25	8.93	
2	5.11	7.23	8.99	
3	5.10	7.19	9.18	
	5.05	8.40	10.30	(24)
	5.27	8.01	12.07	(20)
	4.96			(36)
	5.2			(17)
	4.96			(11)
	4.92			(33)
	4.86			(50)
	4.857			(45)
	4.92			(69)
	5.07			(25)
	4.98			(27)
	5.02			(47)
	5.47			(37)
	4.95			(35)

^aValues reported without a reference are from this work.

Values for the degree of formation, α_n , of the HP_n^{+1} species were calculated using the values of the over-all stoichiometric formation constants, and Equation 27. The value of α_n is the fraction of the total hydrogen ion in the form

of the HP_n^{+1} species. These values have been calculated using average values of the β_n 's obtained in the three trials. The degree of formation plot of α_n vs. $\log (P)$ is shown in Figure 4. It should be noted that the HP_1^{+1} species is the most predominant species except in high concentrations of uncombined 1,10-phenanthroline. As the concentration of 1,10-phenanthroline is increased, the higher order species, HP_2^{+1} and HP_3^{+1} , become more and more significant.

The difference between the α values for the HP_n^{+1} system and those for the CdP_n^{+2} and ZnP_n^{+2} systems, Figures 11 and 12, should be noted. The step formation constants and the over-all formation constants in the MP_n^{+2} systems are orders of magnitude greater than those in the HP_n^{+1} system. This markedly affects the character of the α plot. There is a greater separation of the peaks of the individual MP_n^{+2} species and in the highest concentrations of 1,10-phenanthroline the metal is almost completely in the form of MP_3^{+2} .

It is possible to calculate another type of α value, α' . These may be defined as the fraction of the total 1,10-phenanthroline that is uncombined, α'_u , or in the form of the HP_n^{+1} species, α'_n ,

$$\alpha'_u = \frac{(P)}{(P_T)} \quad (64)$$

$$\alpha'_n = \frac{n(HP_n^{+1})}{(P_T)} \quad (65)$$

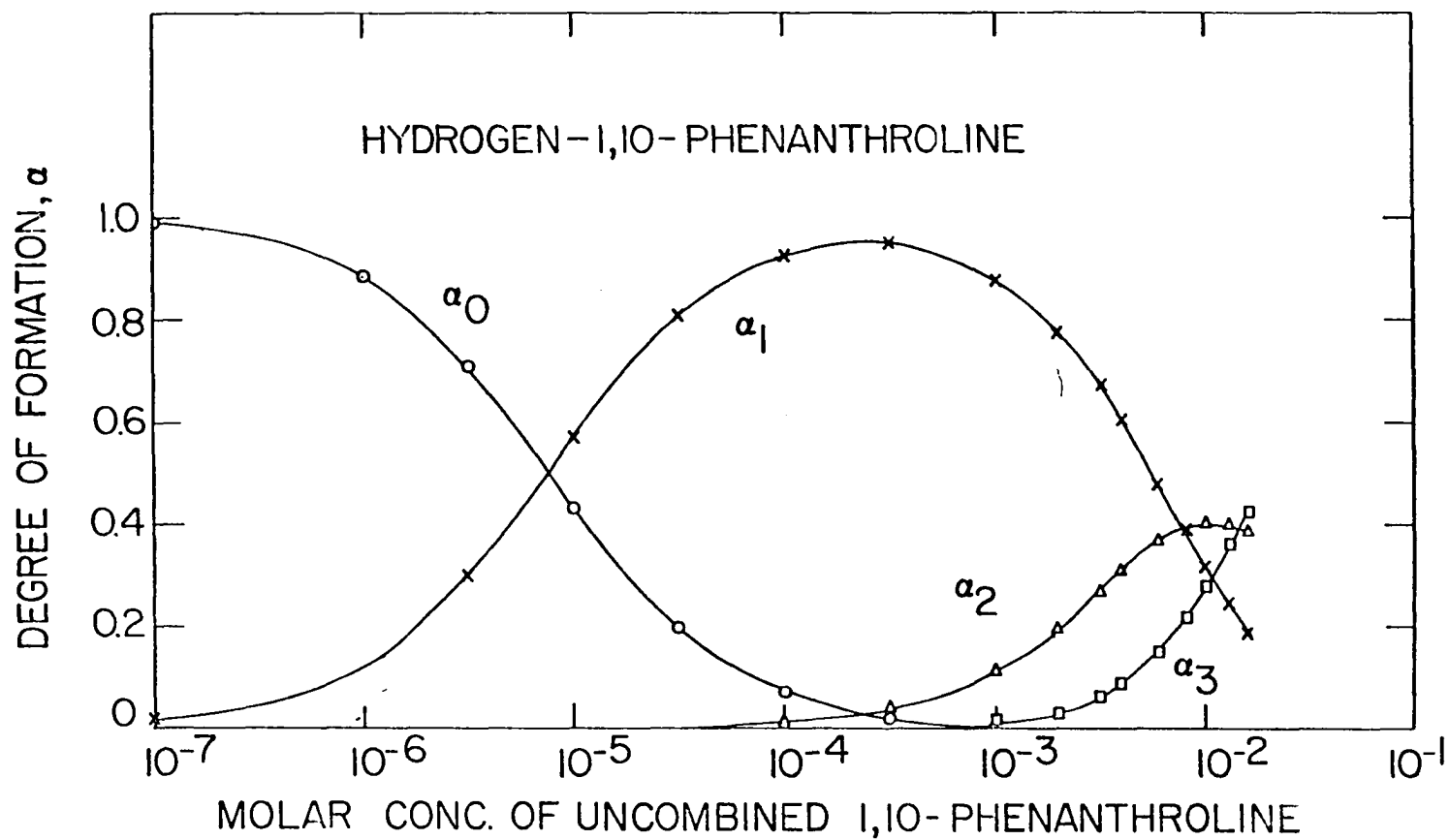


Figure 4. Degree of formation, α , for hydrogen-1,10-phenanthroline

$$= \frac{n\alpha_n(H_T^{+1})}{(P) + (H_T^{+1}) \sum_{n=1}^3 \alpha_n} \quad (66)$$

The α values are a function of the concentration of uncombined 1,10-phenanthroline, but the α' values are also dependent upon the total concentration of hydrogen ion. Values of α' have been calculated at the following concentrations of total hydrogen ion: 1×10^{-3} , 1×10^{-2} and 1×10^{-1} M H_T^{+1} . These values are shown as a function of the concentration of uncombined 1,10-phenanthroline in Figures 5, 6 and 7 respectively.

The results again demonstrate that as the concentration of uncombined 1,10-phenanthroline is increased, the significance of the higher order HP_n^{+1} species becomes greater. Further, at a specific concentration of uncombined 1,10-phenanthroline, the significance of the higher order species is greater the higher the total concentration of hydrogen ion.

To demonstrate the effect the higher order HP_n^{+1} species have on the pH of the system a hypothetical neutralization titration of 100 ml. of 0.01 M 1,10-phenanthroline with a 0.1 M solution of a strong acid was considered. The \bar{n} function, Equation 26, for the HP_n^{+1} system ($N = 3$), was rearranged to a fourth degree polynomial in (P),

$$\sum_{n=0}^4 \left[\beta_n [n(H_T^{+1}) - (P_T)] + \beta_{n-1} \right] (P)^n = 0 \quad (67)$$

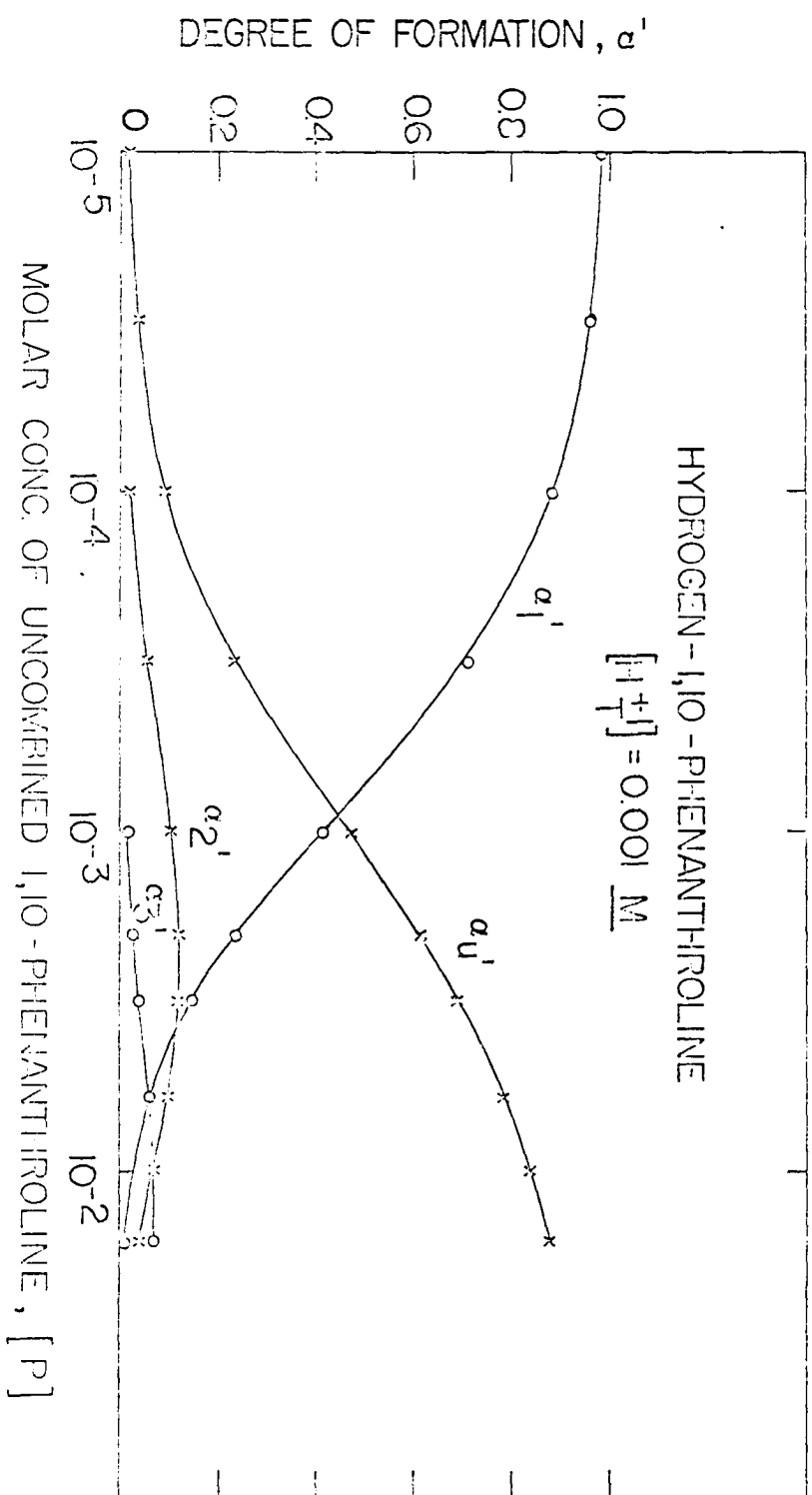


Figure 5. Degree of formation, α' , for hydrogen-1,10-phenanthroline, $(H_p^{+1}) = 0.001 \text{ M}$

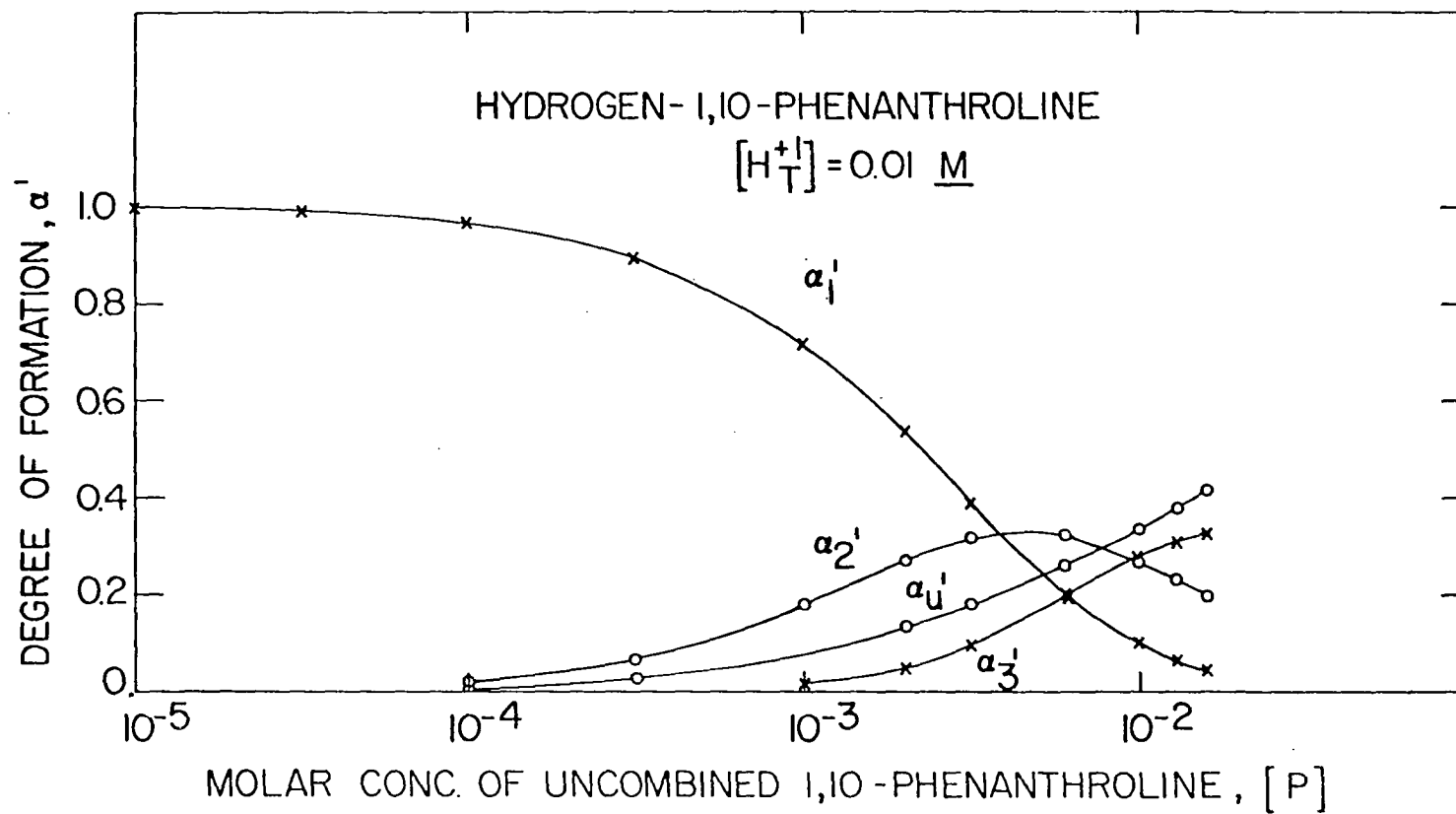


Figure 6. Degree of formation, α' , for hydrogen-1,10-phenanthroline,
 $(H_T^{+1}) = 0.01 \text{ M}$

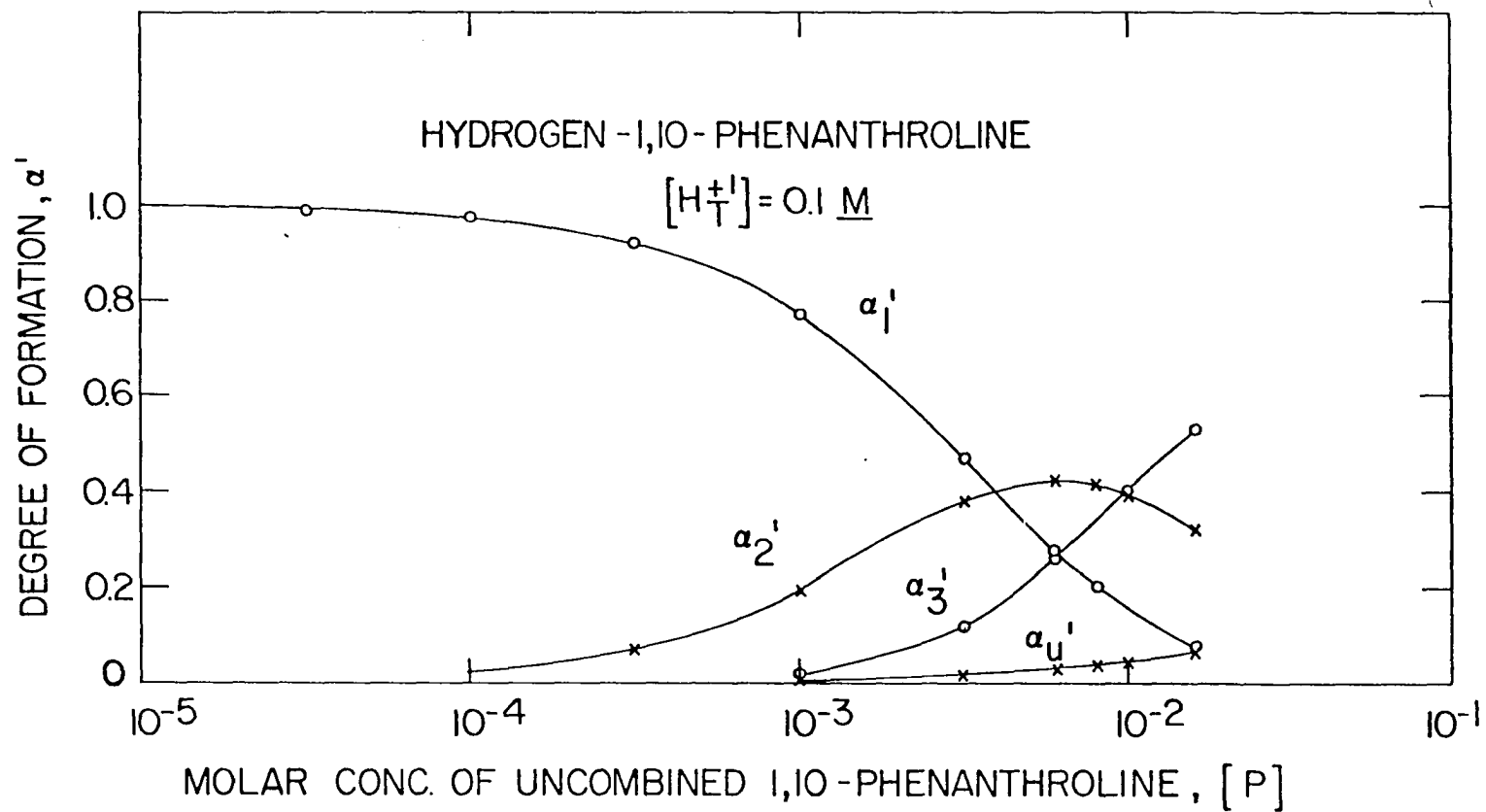


Figure 7. Degree of formation, α' , for hydrogen-1,10-phenanthroline,
 $(H_T^{+1}) = 0.1 \text{ M}$

where, by definition, $\beta_0 = 1$, $\beta_{-1} = 0$ and $\beta_4 = 0$. The roots of the expression for several points along the titration were computed on an IBM 7074 computer by a root finder technique. One real, positive root was obtained for each point. Using the resulting values for (P), values of α_0 for the uncombined hydrogen ion could be calculated using Equation 27. From the values of α_0 the concentration of uncombined hydrogen ion, and hence pH, could be obtained from

$$(H^{+1}) = \alpha_0 (H_T^{+1}) . \quad (68)$$

The resulting plot of pH vs. the ratio of moles of acid added per mole of total 1,10-phenanthroline is compared in Figure 8 to the pH calculated in a similar manner but only the HP_1^{+1} species is considered.

Only a slight difference between the two curves is observed. This occurs in the initial portion of the titration where the concentration of uncombined 1,10-phenanthroline is highest. As the neutralization proceeds the concentration of uncombined 1,10-phenanthroline decreases and the difference between the two curves decreases. The pH values for the case where the higher order species are considered is greater than in the case where only the HP_1^{+1} species is considered. In either case the equivalence point of the titration would be identical.

Lee et al. (36) show a similar plot comparing the experimental and calculated values of pH during a titration of 0.01 M 1,10-phenanthroline with 0.2 M HCl. Their calculated

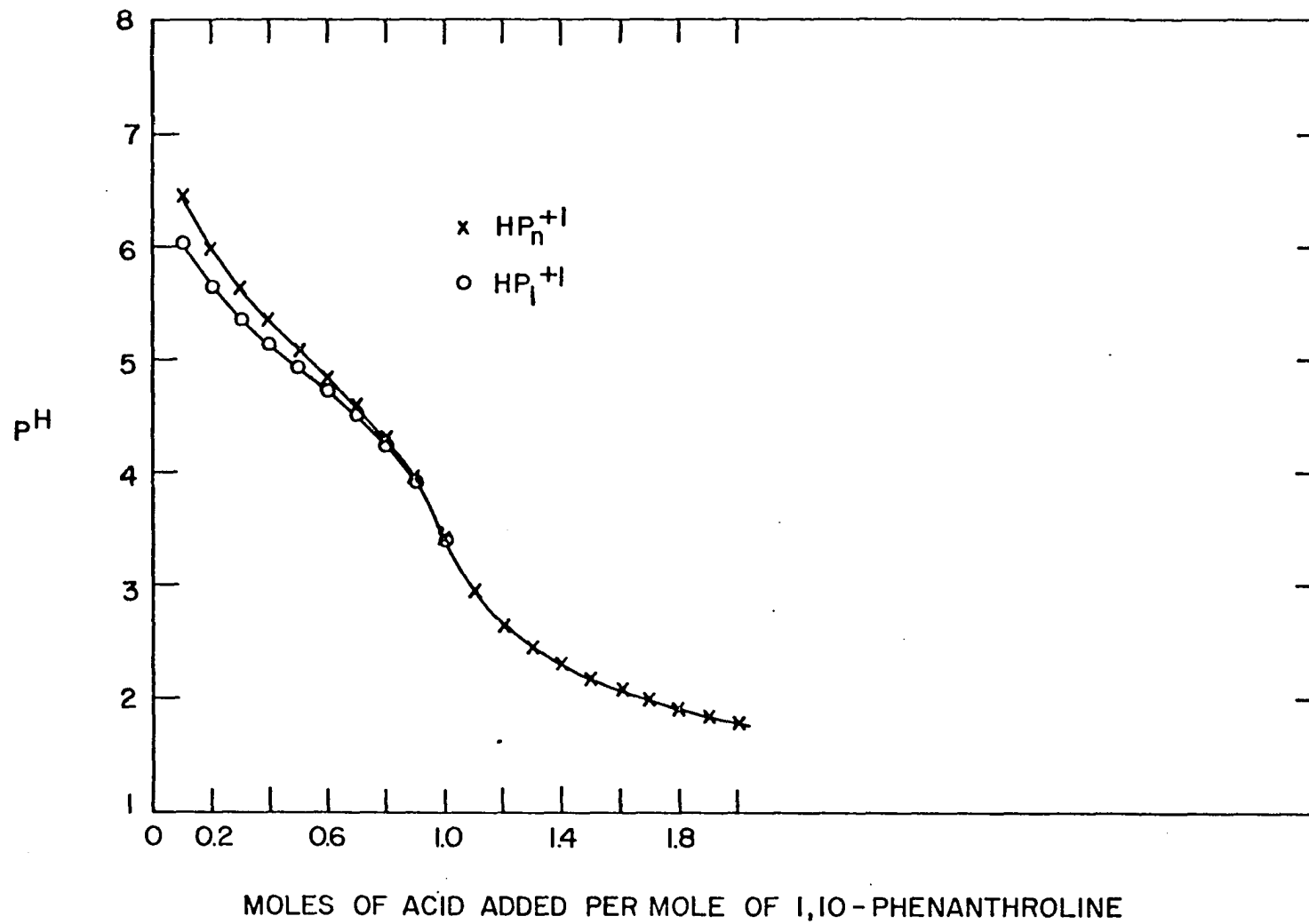
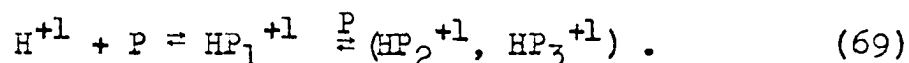


Figure 8. pH study

pH values were obtained by considering only the HP_1^{+1} species. The agreement between the two curves is good except in the initial region of the neutralization where the concentration of uncombined 1,10-phenanthroline is highest. Their experimental pH values are higher than their calculated pH values, as would be the case if the higher order species were present but unaccounted for.

Krumholz (33) determined the pK_a of HP_1^{+1} by a potentiometric titration of 1,10-phenanthroline with HCl. He noted an increase in K_a of about 30% in passing from the beginning to the end of the neutralization reaction. He noted that a similar trend in K_a was visible in the titration curve presented by Lee *et al.* (36). This increase in K_a may also be explained by considering the higher order species. This can best be illustrated by considering the reaction for the formation of the HP_1^{+1} species,



The formation of the higher order species would tend to drive this reaction toward the right thereby decreasing the experimentally measured concentration of uncombined hydrogen ion (increasing the pH) and making the β_1 appear greater than it actually is. The higher order species are more significant the greater the concentration of uncombined 1,10-phenanthroline, therefore β_1 would seem largest at the beginning of the titration. As the neutralization proceeds, the concen-

tration of uncombined 1,10-phenanthroline would decrease and the value of β_1 would decrease to its actual value. The acid dissociation constant for the HP_1^{+1} species is the reciprocal of β_1 , hence, it would appear lowest at the beginning of the titration and it would increase to its actual value as the neutralization proceeds.

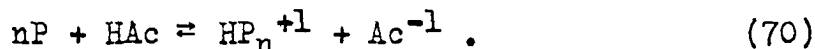
I. The Over-all Formation Constants of the Cadmium- and Zinc-1,10-phenanthroline Complexes

The MP_n^{+2} systems were studied to show the scope and to check the reliability of the experimental and computational methods. The CdP_n^{+2} and ZnP_n^{+2} systems were chosen because the values of β_n for these complexes have been determined by a number of other workers. The values of β_n obtained in this work could be compared with their reported results.

The values of β_n for the MP_n^{+2} systems were determined in a manner analogous to that used in the study of the HP_n^{+1} system. Since the CdP_n^{+2} and ZnP_n^{+2} complexes are considerably more stable than the HP_n^{+1} species, the standard electrode response plot was prepared to about an order of magnitude lower in the concentration of uncombined 1,10-phenanthroline. To aid in extending this lower limit a higher concentration of KNO_3 (1.000×10^{-2} M) was employed in the system. For the study of the CdP_n^{+2} system both solutions used in the titration contained 1.079×10^{-3} M $CdSO_4$ and in the ZnP_n^{+2} study both solutions contained

$1.080 \times 10^{-3} \text{ M ZnSO}_4$. The medium was buffered at a pH of about 4.6 with a 0.0100 M acetic acid and 0.0100 M potassium acetate buffer. The ionic strength was maintained at 0.1 with K_2SO_4 . The titrant solutions contained about $1.5 \times 10^{-2} \text{ M}$ 1,10-phenanthroline. Two experimental trials were conducted on each MP_n^{+2} system.

In the MP_n^{+2} studies it was noticed that the pH of the titration medium increased by about two or three tenths of a pH unit from the beginning to the end of the titration. This change could have been reduced by employing a medium with a greater buffer capacity. Instead the actual pH values were calculated for each experimental datum point. The change in pH was due to the following reaction between 1,10-phenanthroline and acetic acid, HAc,



The total concentration of the HP_n^{+1} species can be calculated from

$$\sum_{n=1}^3 (\text{HP}_n^{+1}) = (\text{H}^{+1}) \sum_{n=1}^3 \beta_n (\text{P})^n \quad (71)$$

by assuming an initial value for (H^{+1}) . A better estimate of the (H^{+1}) or pH was then obtained from

$$\text{pH} = \text{pK}_a - \log \frac{(\text{HAc}') - \sum_{n=1}^3 (\text{HP}_n^{+1})}{(\text{Ac}^{-1}') + \sum_{n=1}^3 (\text{HP}_n^{+1})} \quad (72)$$

where K_a is the acid dissociation constant of acetic acid (40) and (HAc') and (Ac^{-1}') are the initial concentrations of acetic acid and potassium acetate respectively. The iteration was conducted until successive values of pH agreed to within 0.001 pH unit. The calculated pH values agreed well with some experimental values.

The total concentration of 1,10-phenanthroline combined with the hydrogen ion for each datum point in the MP_n^{+2} studies can then be determined from

$$\sum_{n=1}^3 n(HP_n^{+1}) = (H^{+1}) \sum_{n=1}^3 n\beta_n(P)^n. \quad (73)$$

In this manner the experimental data in the MP_n^{+2} studies were corrected for the HP_n^{+1} species. This correction must be made before the computer computations are performed in order to obtain meaningful results. If this correction is not made before the computations are performed, some experimental values of \bar{n} will exceed three. The computer then attempts to describe experimental data, that appears to be from a four-parameter experimental system, with a three-parameter program and spurious results are obtained.

The total concentration of 1,10-phenanthroline not combined with hydrogen ion, (P_T') , in the MP_n^{+2} system is

$$(P_T') = (P_T) - \sum_{n=1}^3 n(HP_n^{+1}). \quad (74)$$

The \bar{n} function for the MP_n^{+2} system is

$$\bar{n} = \frac{(P_T) - \sum_{n=1}^3 n(HP_n^{+1}) - (P)}{(M_T^{+2})} = \frac{(P_T') - (P)}{(M_T^{+2})} \quad (75)$$

and the rearranged \bar{n} function used in the weighted least squares computer program is

$$\sum_{n=0}^3 \beta_n(P)^n [(P_T') - (P) - n(M_T^{+2})] = 0 \quad (76)$$

Figure 9 compared a plot of \bar{E} vs. $\log (P_T)$ for the CdP_n^{+2} and ZnP_n^{+2} investigations with that obtained in the HP_n^{+1} investigation. The progress of the titrations on the CdP_n^{+2} and ZnP_n^{+2} systems are shown in Tables 7-10. The quantities, \bar{E} and \bar{P} , are the average values of the Ag/AgP_2NO_3 electrode potentials and the average values of the concentrations of uncombined 1,10-phenanthroline determined by the five Ag/AgP_2NO_3 electrodes. The values for the experimental \bar{n} , \bar{n}_e , were calculated from Equation 75 and the values for the calculated \bar{n} , \bar{n}_c , were obtained on the computer from Equation 41 using the previously determined values for β_n' .

The resulting values of the over-all conditional formation constants, β_n' , for the CdP_n^{+2} and ZnP_n^{+2} complexes with their estimated standard deviations are listed in Table 11. The values of β_n' have, of necessity, been corrected for the HP_n^{+1} species.

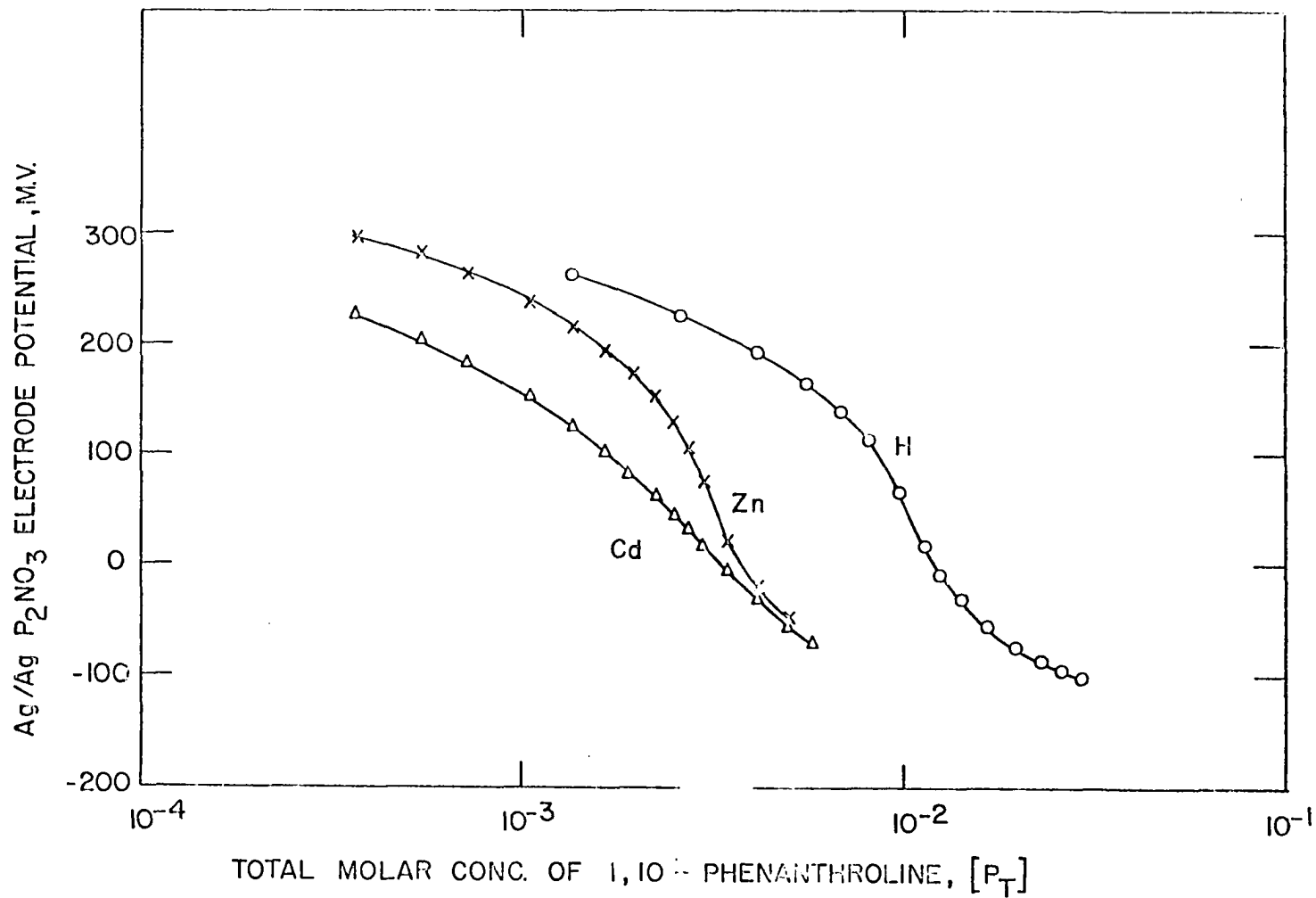


Figure 9. Titrations of hydrogen, cadmium and zinc ions with 1,10-phenanthroline

Table 7. The titration of cadmium(II) with 1,10-phenanthroline, trial 1^a

Titrant (ml.)	$P_T \times 10^3$ (<u>M</u>)	\bar{E} (mv.)	\bar{P} (<u>M</u>)	\bar{n}_e	\bar{n}_c
1.00	0.3659	232.4	1.21×10^{-6}	0.33	0.34
1.50	0.5421	209.9	1.92	0.49	0.49
2.00	0.7143	190.8	2.86	0.65	0.65
3.00	1.047	161.8	5.24	0.95	0.94
4.00	1.364	137.8	8.55	1.23	1.21
5.00	1.667	114.1	1.43×10^{-5}	1.51	1.50
6.00	1.875	94.3	2.15	1.73	1.74
7.00	2.234	75.1	3.24	1.95	1.96
8.00	2.500	58.7	4.59	2.14	2.14
9.00	2.755	43.4	6.49	2.28	2.31
10.00	3.000	28.9	8.86	2.44	2.44
12.00	3.462	4.0	1.53×10^{-4}	2.64	2.62
15.00	4.091	-22.7	2.78	2.78	2.77
20.00	5.000	-48.7	4.99	2.87	2.86
25.00	5.769	-63.9	7.11	2.92	2.90

^aThe titrant solution contained 0.01500 M 1,10-phenanthroline.

Table 8. The titration of cadmium(II) with 1,10-phenanthroline, trial 2^a

Titrant (ml.)	$P_T \times 10^3$ (M)	\bar{E} (mv.)	\bar{P} (M)	\bar{n}_e	\bar{n}_c
1.00	0.3659	234.4	1.12×10^{-6}	0.33	0.34
1.50	0.5421	210.2	1.81	0.50	0.48
2.00	0.7143	191.2	2.85	0.65	0.65
2.50	0.8824	175.2	3.99	0.80	0.80
3.00	1.047	161.4	5.31	0.95	0.93
4.00	1.273	137.6	8.75	1.23	1.19
5.00	1.667	115.5	1.37×10^{-5}	1.49	1.45
6.00	1.957	95.5	2.09	1.73	1.72
7.00	2.234	76.8	3.11	1.95	1.98
8.00	2.500	58.5	4.52	2.17	2.20
9.00	2.755	44.7	6.29	2.33	2.38
10.00	3.000	31.4	8.40	2.46	2.51
12.00	3.462	7.5	1.42×10^{-4}	2.68	2.69
15.00	4.091	-18.4	2.51	2.87	2.82

^aThe titrant solution contained 0.01500 M 1,10-phenanthroline.

Table 9. The titration of zinc(II) with 1,10-phenanthroline, trial 1^a

Titrant (ml.)	$P_T \times 10^3$ (M)	\bar{E} (mv.)	\bar{P} (M)	\bar{n}_e	\bar{n}_c
1.00	0.3683	296.2	3.35×10^{-7}	0.34	0.36
1.50	0.5458	282.0	4.51	0.50	0.48
2.00	0.7190	264.5	6.46	0.66	0.65
3.00	1.053	243.0	1.02×10^{-6}	0.97	0.94
4.00	1.373	221.7	1.58	1.26	1.25
5.00	1.678	201.3	2.41	1.54	1.55
6.00	1.970	181.2	3.68	1.81	1.82
7.00	2.249	159.5	5.75	2.06	2.07
8.00	2.517	136.3	9.31	2.29	2.30
9.00	2.773	112.6	1.54×10^{-5}	2.51	2.50
10.00	3.020	84.5	2.76	2.69	2.67
12.00	3.485	26.1	9.36	2.87	2.89
15.00	4.118	-19.9	2.53×10^{-4}	2.88	2.96
20.00	5.033	-51.2	4.97	2.92	2.98

^aThe titrant solution contained 0.01510 M 1,10-phenanthroline.

Table 10. The titration of zinc(II) with 1,10-phenanthroline, trial 2^a

Titrant (ml.)	$P_T \times 10^5$ (\underline{E})	\bar{E} (mv.)	\bar{P} (\underline{M})	\bar{n}_e	\bar{n}_c
1.00	0.3673	297.6	3.14×10^{-7}	0.34	0.38
1.50	0.5443	284.5	4.07	0.50	0.48
2.00	0.7171	269.0	5.58	0.65	0.63
3.00	1.051	244.3	9.36	0.97	0.93
4.00	1.369	222.7	1.48×10^{-6}	1.26	1.25
5.00	1.673	202.2	2.25	1.54	1.56
6.00	1.954	182.8	3.40	1.81	1.84
7.05	2.257	163.1	5.05	2.07	2.08
8.00	2.510	143.6	7.75	2.29	2.30
9.00	2.766	120.7	1.24×10^{-5}	2.52	2.50
10.00	3.012	90.0	2.37	2.70	2.70
12.00	3.475	32.7	8.20	2.91	2.90

^aThe titrant solution contained $0.0150\% \pm$ 1,10-phenanthroline.

Table 11. Over-all conditional formation constants of the cadmium- and zinc-1,10-phenanthroline complexes^a

Metal	Trial	$\log \beta_1'$	$\log \beta_2'$	$\log \beta_3'$
Cd	1	5.55 ± 0.02	10.40 ± 0.02	14.53 ± 0.02
	2	5.60 ± 0.03	10.33 ± 0.04	14.65 ± 0.04
Zn	1	6.03 ± 0.04	11.83 ± 0.03	16.76 ± 0.03
	2	6.11 ± 0.03	11.88 ± 0.03	16.95 ± 0.03

^aValues have been corrected for the HP_n^{+1} species but not for the metal acetate or metal sulfate complexes, $\mu = 0.1$, $t = 25^\circ \pm 0.05^\circ C$.

The values of the over-all stoichiometric formation constants, β_n , were obtained by correcting the conditional formation constants for the metal acetate (31) and metal sulfate (15,46,68) complexes. The results are shown in Table 12 with the values of β_n reported by other workers.

The formation function curves, which show the agreement between the values of \bar{n}_e and \bar{n}_c , for the CdP_n^{+2} and ZnP_n^{+2} systems are compared in Figure 10 to the formation function curve obtained in the HP_n^{+1} study. The degree of formation curves for the CdP_n^{+2} and ZnP_n^{+2} systems calculated from Equation 27 using the over-all constants are shown in Figures 11 and 12 respectively.

J. Solubility Study

Rossotti and Rossotti (49) have reviewed the utility of solubility studies in the investigation of complex equilibria.

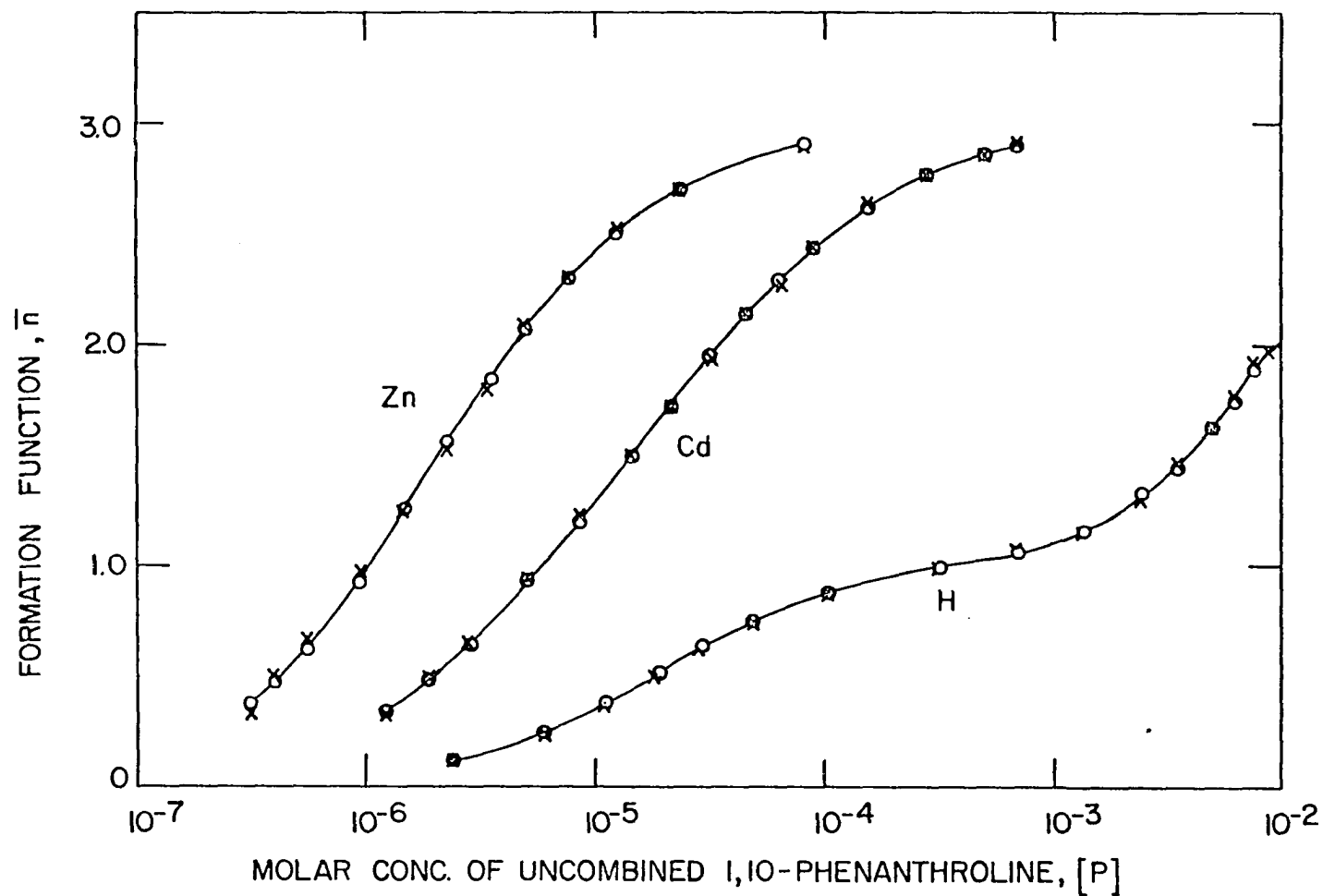


Figure 10. Formation function for hydrogen-, cadmium- and zinc-1,10-phenanthroline; o, calculated \bar{n} ; x, experimental \bar{n}

Table 12. Over-all stoichiometric formation constants of the cadmium- and zinc-1,10-phenanthroline complexes^a

Metal	Trial	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Reference
Cd	1	5.88	10.74	14.87	
	2	5.93	10.66	14.98	
		5.93	10.52	14.30	(13)
		5.75	10.84	13.91	(20)
		5.17	10.0	14.26	(27)
		6.01 (1)		15.19 (16)	(1,16)
Zn	1	6.32	12.12	17.03	
	2	6.39	12.16	17.24	
		6.83	12.05	16.92	(13)
		6.31	12.40	17.17	(20)
		6.30	11.95	17.05	(27)
		6.36	12.00	17.00	(4)
		6.5	11.95	17.05	(26)
		6.43	12.15	17.0	(32)
		6.47	12.00	13.1	(42)

^aValues reported without a reference were obtained in this work.

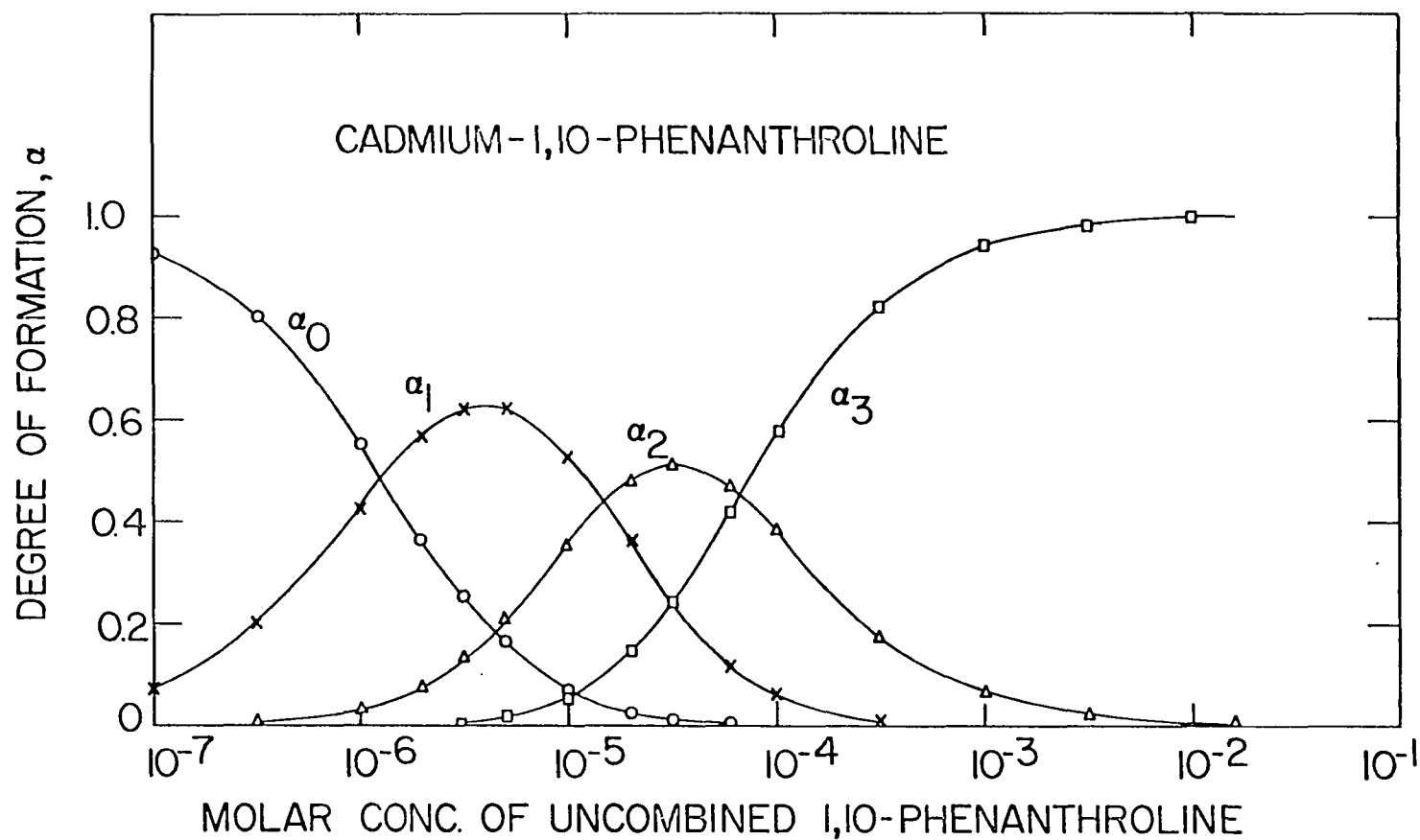


Figure 11. Degree of formation, α , for cadmium-1,10-phenanthroline

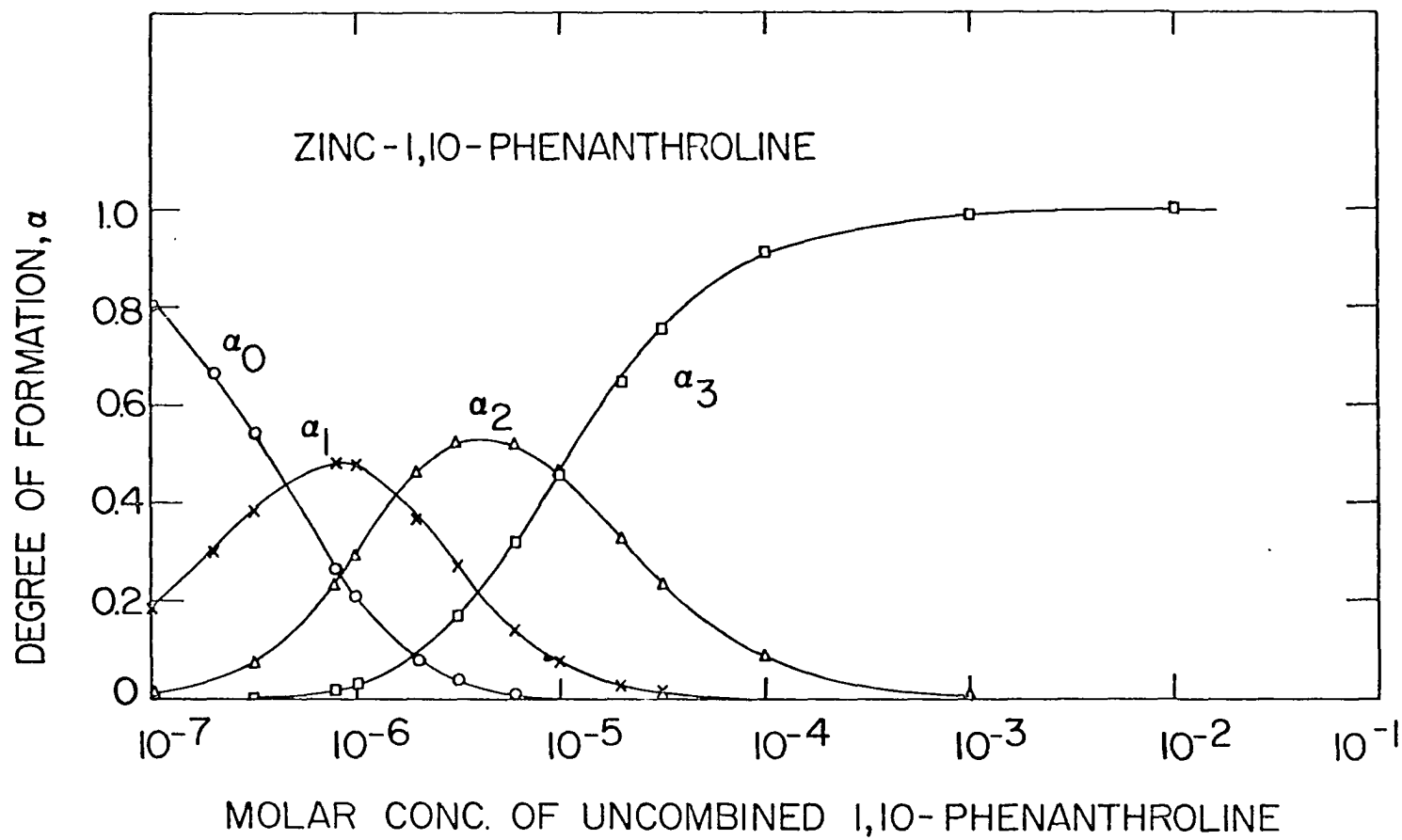


Figure 12. Degree of formation, α , for zinc-1,10-phenanthroline

The solubility, S_A , of a sparingly soluble ligand, A, in the presence of a central metal ion, B, is

$$S_A = S_A^0 + \sum_{n=1}^N n(BA_n) \quad (77)$$

which is analogous to

$$A = a + \sum_{n=1}^N n(BA_n) \quad (78)$$

Upon considering the \bar{n} equation, Equation 26, it can be shown that

$$S_A = S_A^0 + \bar{n}_s (B) \quad (79)$$

where S_A^0 is the solubility of the ligand or the concentration of uncombined ligand, a, in the absence of the central metal ion and \bar{n}_s , \bar{n} saturated, is the value of the \bar{n} function for the BA_n system when the system is saturated with the ligand,

$$\bar{n}_s = \frac{\sum_{n=1}^N n \beta_n (S_A^0)^n}{1 + \sum_{n=1}^N \beta_n (S_A^0)^n} \quad (80)$$

Hence, the solubility of a sparingly soluble ligand in the presence of the central metal ion should be a linear function of the total concentration of the metal ion with a slope of \bar{n}_s .

The value of \bar{n}_s for the HP_n^{+1} system may be calculated from the values for β_n and a value for the solubility of 1,10-phenanthroline in water. The solubility of 1,10-phenan-

throline in water has been determined by Grimes (24), Smith and Richter (54) and this author. An average value is 0.0160 M. This ligand solubility determined in the absence of any central metal ion is essentially the maximum value of uncombined 1,10-phenanthroline that can be attained in an aqueous medium. This would also be the concentration of uncombined 1,10-phenanthroline in solutions, containing a central metal ion, which are saturated in 1,10-phenanthroline. The corresponding value of \bar{n}_s for the HP_n^{+1} system calculated from Equation 80 with $S_A^0 = 0.0160$ M is 2.23. This value of \bar{n}_s is the maximum attainable value of \bar{n} in the HP_n^{+1} system which is realized only in solutions that are saturated in 1,10-phenanthroline.

The solubility of 1,10-phenanthroline in aqueous acidic medium has been measured by Grimes (24) and in the present work. A series of aqueous solutions of hydrochloric acid (0 to 0.0526 M) were shaken at 25°C with an excess of solid 1,10-phenanthroline. A portion of the saturated supernate was withdrawn, diluted and made neutral. The concentration of 1,10-phenanthroline, and hence its solubility, was determined by ultraviolet spectrophotometry at 265 $m\mu$. In the work by Grimes (24) the solubility was determined by a conductometric titration with standardized acid. The nature of this conductometric titration has previously been described.

In all four experimental trials, two by Grimes (24) and two by this author, a linear plot of solubility of 1,10-

phenanthroline vs. the total concentration of hydrochloric acid was obtained. In the four trials the ionic strength was controlled only in one trial by the present author ($\mu = 0.1$ with KCl). This author has performed a least squares method on the four sets of data to determine the slope of each of the solubility plots. The resulting slope values are listed in Table 13 with the range in concentration of hydrochloric acid used in each trial.

Table 13. Slope of the experimental solubility plots for 1,10-phenanthroline^a

Worker	Trial	Range HCl(M)	Experimental slope
Fahsel	1 ^b	0-0.0526	2.23
	2	0-0.0526	2.24
Grimes	1	0-0.238	2.14
	2	0-0.2535	2.47

^a $t = 25^{\circ}\text{C.} \pm 0.05^{\circ}\text{C.}$

^bValue obtained at $\mu = 0.1$ (KCl).

Values of \bar{n}_s for the HP_n^{+1} system have been calculated from the values of β_n determined in this work and from those reported by Grimes (24) and Fullerton (20) using Equation 80. The results were: Fahsel, 2.23; Grimes, 2.53; and Fullerton, 2.98. These values of \bar{n}_s should be compared with the experimental solubility slope values listed in Table 13. Figure 13 shows the agreement between the experimental solubility of

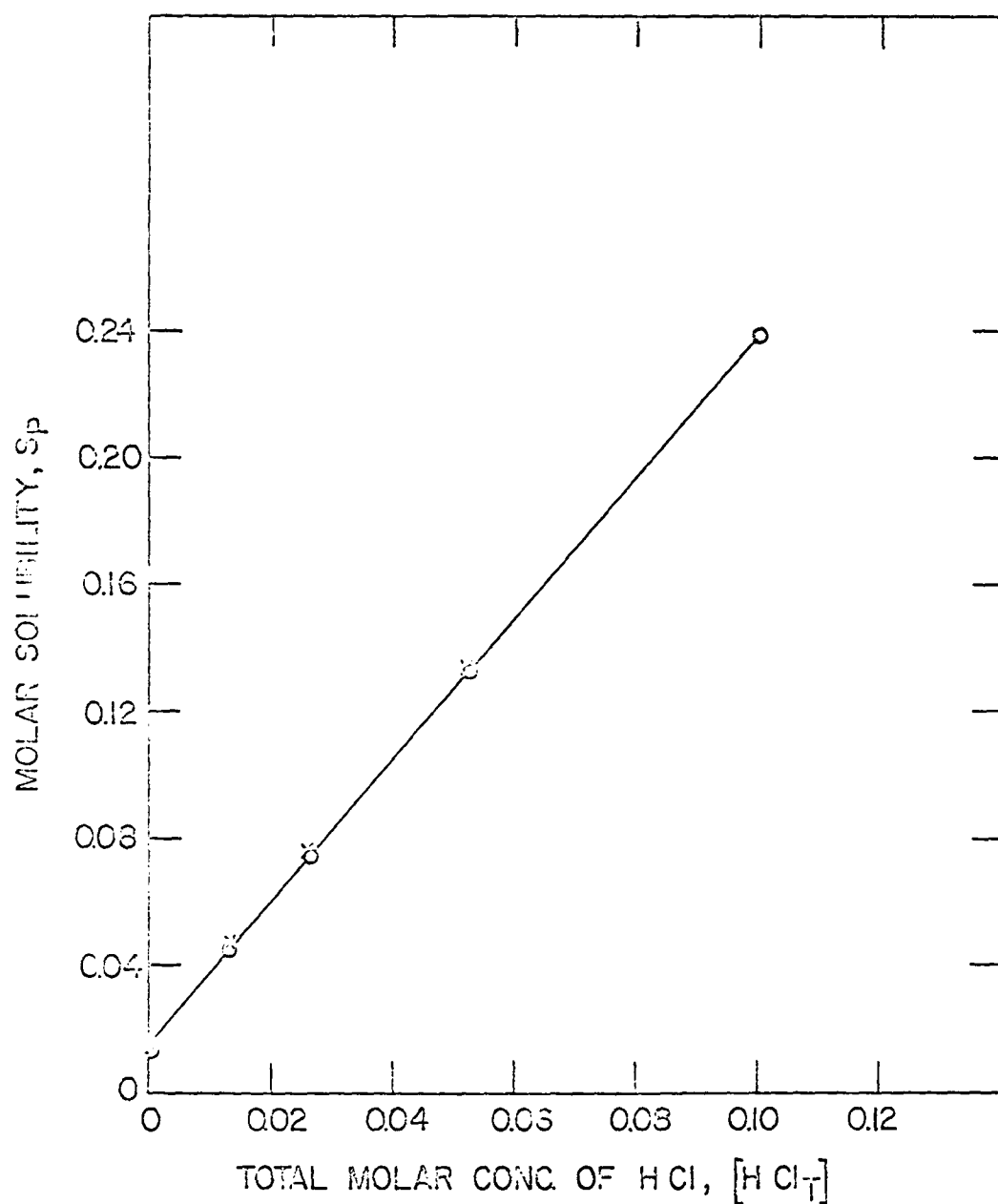


Figure 13. Solubility study of 1,10-phenanthroline; curve, $S_p^0 + \bar{n}_s(H_T^{+1})$; x, $\mu = 0.1$; o, μ not controlled

1,10-phenanthroline and the solubility curve calculated from Equation 79 using the values of β_n determined in this work.

This increase in solubility is by no means trivial. If one compares the solubility of 1,10-phenanthroline in water (0.0160 M) to that in 0.1 M HCl (0.239 M), a fifteenfold increase in solubility is observed. This increase in solubility is far greater than would be expected from "salting-in" type phenomena (38).

The solubility of 1,10-phenanthroline in water determined in this work was 0.0165 M. The solubility in 0.1 M KCl was somewhat less, 0.0162 M. An increase in solubility would have been expected if complexation of potassium by 1,10-phenanthroline had occurred. This is further evidence that potassium ion is not significantly complexed by 1,10-phenanthroline. This latter result is similar to the "salting-in" behavior reported by Long and McDevit (38). They indicate that potassium chloride "salts out" the basic nonelectrolytes (ammonia, trimethylamine, and aniline) with a "salting-in" parameter, k_s , of about 0.1. This type of behavior is usually described by the Setschenow equation,

$$\log \frac{f}{f^0} = \log \frac{S^0}{S} = k_s C_s \quad (81)$$

where f and f^0 and S and S^0 are the activity coefficients and solubilities of the nonelectrolyte in the salt solution of concentration, C_s , and in water respectively. This equation would predict about a 2% decrease in solubility of a basic

nonelectrolyte in a 0.1 M KCl solution compared to its solubility in water. This is approximately what was observed experimentally for 1,10-phenanthroline as was noted above.

The solubilities of several substituted 1,10-phenanthrolines as a function of the total concentration of HCl were determined in a manner analogous to that used in the 1,10-phenanthroline study. The resulting plots of solubility vs. (HCl_T) are shown in Figure 14. The values for the slopes of these solubility plots are listed in Table 14 in order of decreasing basicity of the substituted 1,10-phenanthroline. The pK_a values listed are a consistent set of values reported by Brandt and Gullstrom (11) and Schilt and Smith (50) for the HP^{+1} species.

Table 14. Slopes of the experimental solubility plots for some substituted 1,10-phenanthrolines^a

Substituted 1,10-phenanthroline	Slope	pK_a^b
2,9-dimethyl-	1.64	6.17
5-methyl-	2.64	5.23
unsubstituted ($\mu = 0.1$)	2.23	4.96
unsubstituted	2.24	4.96
5-chloro-	1.69	4.26
5-nitro-	0.49	3.57

^aValues obtained at $25^\circ \pm 0.05^\circ\text{C}$. Except where noted the ionic strength was not controlled.

^b pK_a values reported by Brandt and Gullstrom (11) and Schilt and Smith (50).

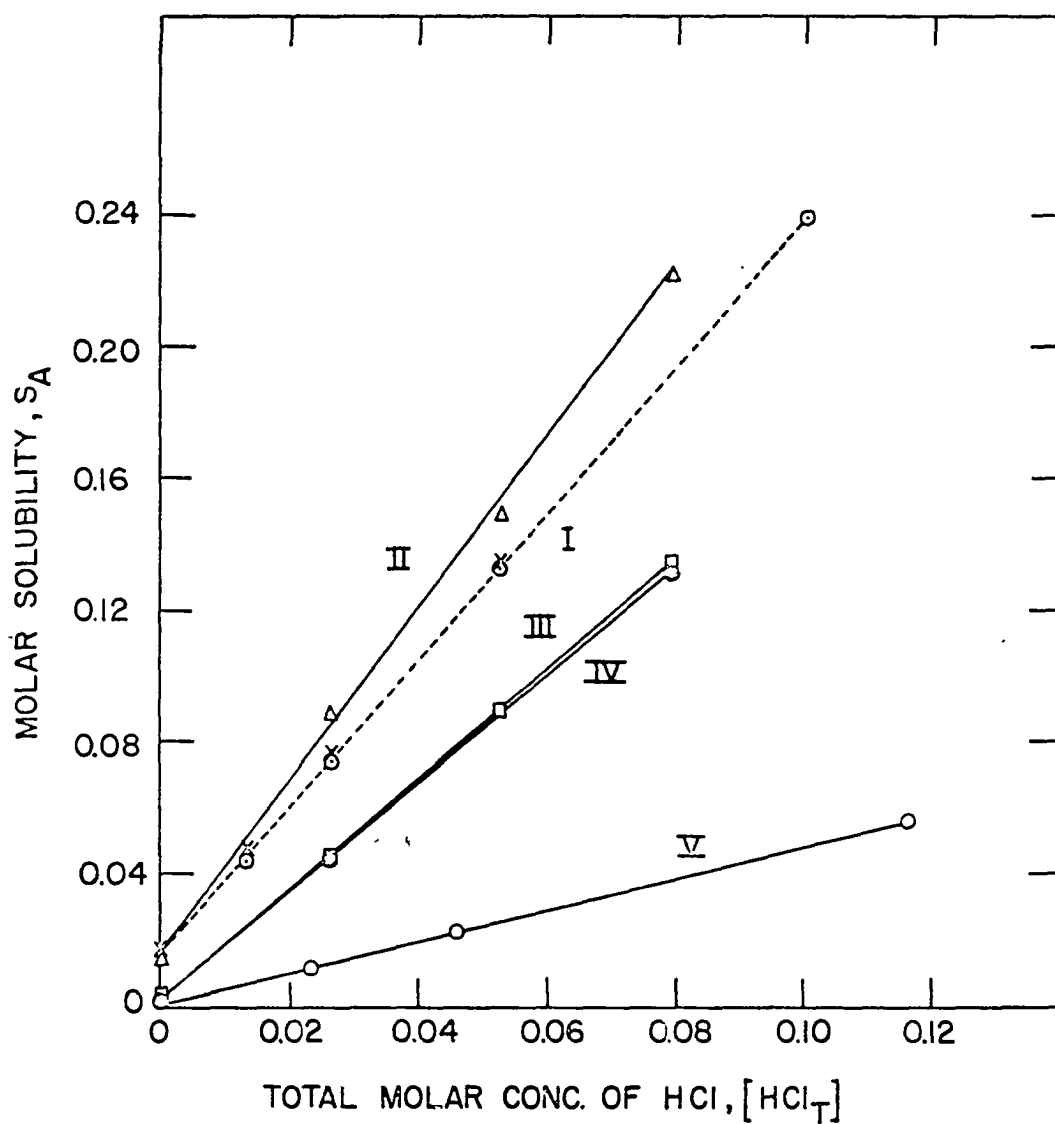


Figure 14. Solubility study of some substituted 1,10-phenanthrolines: I, 1,10-phenanthroline; II, 5-methyl-; III, 5-chloro-; IV, 2,9-dimethyl-; and V, 5-nitro-1,10-phenanthroline

An experimental slope value greater than one indicates that the substituted ligand forms the higher order HP_n^{+1} species. These experimental results indicate that the formation of higher order species is not peculiar to the parent 1,10-phenanthroline. Further, the more basic the substituted 1,10-phenanthroline the higher the solubility slope or the greater the average number of ligand molecules interacting with the hydrogen ion. The 2,9-dimethyl-1,10-phenanthroline is the exception. Undoubtedly steric factors cause it to be out of line.

The 5-nitro-1,10-phenanthroline was the only substituted ligand studied which had a slope less than one. This ligand was further studied to see if any abnormal effects were influencing its behavior. These studies will be described below.

It has been shown that the maximum \bar{n} that may be attained in the hydrogen-1,10-phenanthroline system in an aqueous medium is 2.23. This limitation is a result of the relatively low solubility of 1,10-phenanthroline in aqueous medium. The solubility of 1,10-phenanthroline or the concentration of uncombined 1,10-phenanthroline may be increased by using a mixed-solvent system. It follows then that the maximum attainable \bar{n} should be increased by using a mixed-solvent system. About a tenfold increase in solubility was realized by using a 20% dioxane-water solvent. The solubility of 1,10-phenanthroline as a function of the total concentration of

hydrochloric acid in 20% dioxane-water was determined. The solubility plot was linear with a slope of 3.1. The \bar{n}_s value determined using Equation 80 was 2.9. The agreement between the two values is good considering that one is using the values of β_n of the HP_n^{+1} species that have been determined in an aqueous system to describe an experimental solubility study in a mixed-solvent system. The results obtained in this study substantiate that three and only three HP_n^{+1} species are formed between hydrogen ion and 1,10-phenanthroline.

K. Infrared Study

The infrared spectra of several aqueous solutions containing 2 M 1,10-phenanthroline and 1 to 6 M HCl were obtained using a 0.015 mm. cell with Irtran 2 windows and a Beckman IR-7 infrared spectrophotometer. Water has several broad infrared bands which render much of the infrared region useless but there are a few "windows" where water is transparent enough that usable spectra can be obtained. In the region from about 1100 to 1600 cm^{-1} good infrared spectra of aqueous 1,10-phenanthroline solutions were obtained.

There were several spectral differences between the solution having a $(P_T)/(H_T^{+1})$ ratio of two compared to a solution having a ratio of one. New bands appeared at 1143, 1508 and 1565 cm^{-1} and the band at 1422 cm^{-1} increased in intensity. The changes are in a region characteristic of ring vibrations of aromatic compounds (51). The infrared spectra of these

two solutions from 1100 cm^{-1} to about 1570 cm^{-1} are shown in Figure 15.

Mole-ratio plots of the ratio of the absorbance of the bands at 1422 and 1508 cm^{-1} to that for a band whose absorbance is not changing (1537 cm^{-1}) vs. the ratio, $(P_T)/(HCl_T)$, were prepared. The resulting mole-ratio plots are shown in Figure 16. They also indicate that higher order species are forming since the changes in absorbance are directly proportional to the $(P_T)/(HCl_T)$ ratio when the ratio is greater than one. The plots might be more informative if the $(P_T)/(HCl_T)$ ratio could be extended to higher values but one is limited by the limited solubility of 1,10-phenanthroline. Another solvent system, particularly a mixed-solvent system that is principally aqueous, might be beneficial. The solvent system would need to be one in which the solubility of 1,10-phenanthroline is considerably greater, it must be transparent in the infrared region of interest and it must not significantly affect the HP_n^{+1} system.

L. Study of 5-Nitro-1,10-phenanthroline

Of the substituted 1,10-phenanthrolines investigated in the solubility study 5-nitro-1,10-phenanthroline, nP, was unique in that the slope of its solubility plot was less than one. The slope was 0.49. To determine whether any abnormal species, perhaps H_2P^{+2} , were being formed some further studies were performed.

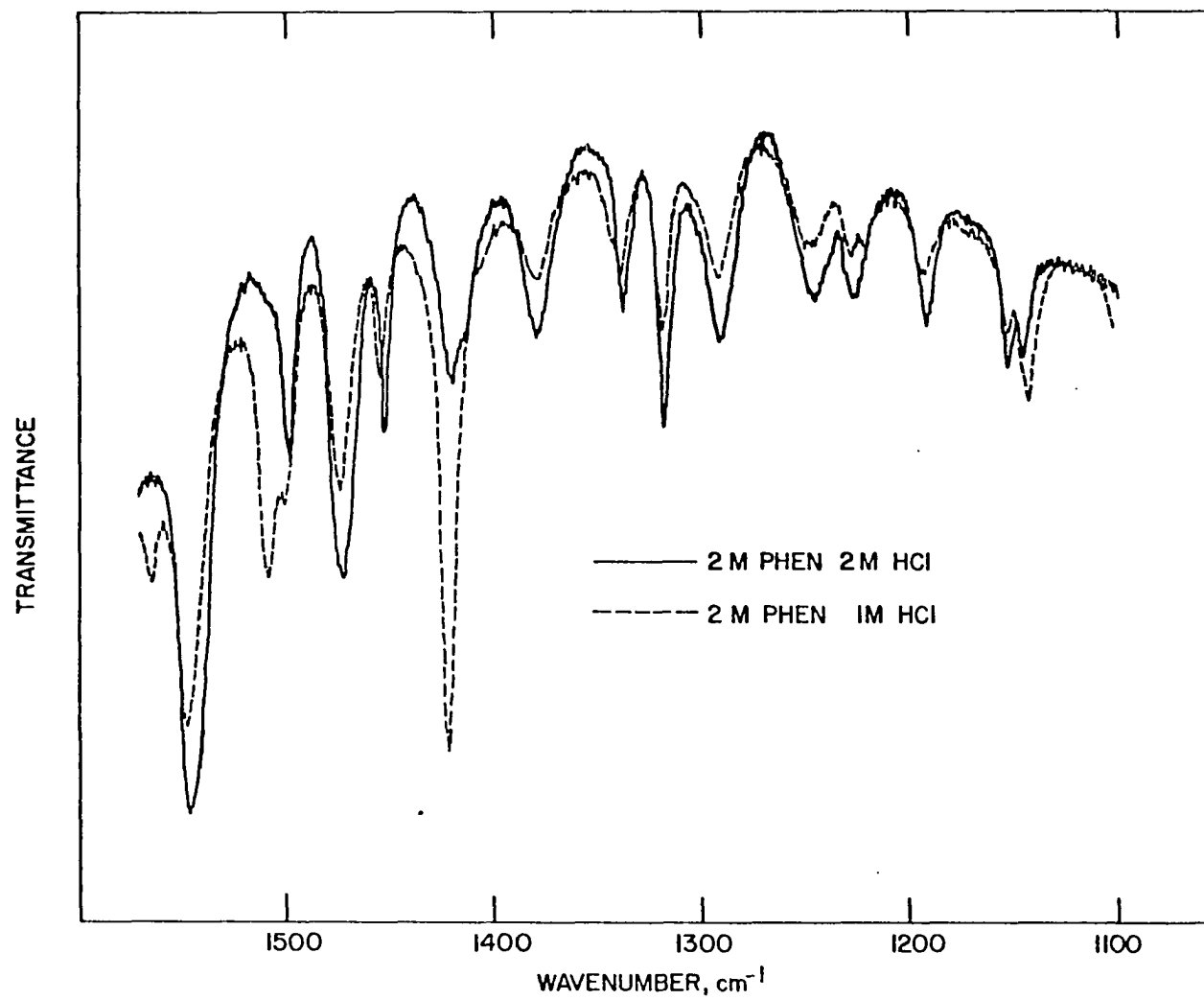


Figure 15. Infrared spectra of hydrogen-1,10-phenanthroline

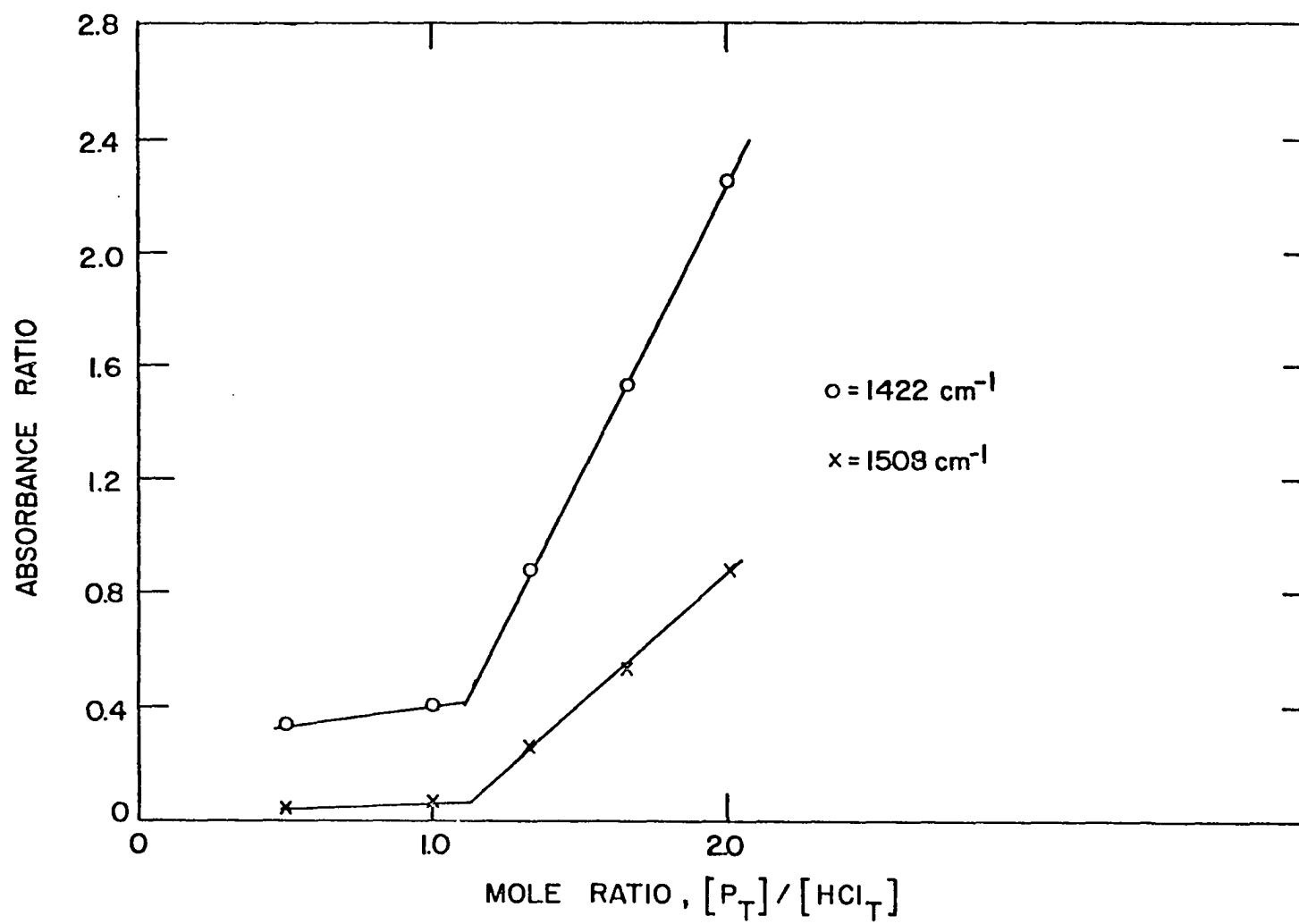
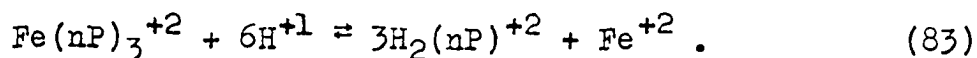
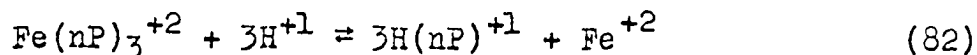


Figure 16. Mole-ratio plot of hydrogen-1,10-phenanthroline

An equilibrium study, similar to that used by Lee et al. (36) in their investigation of 1,10-phenanthroline, was conducted. In acidic solution two possible reactions were considered for the dissociation of the complex, tris(5-nitro-1,10-phenanthroline)iron(II), $\text{Fe}(\text{nP})_3^{+2}$,



The equilibrium constant for Equation 82, K_1 , is

$$K_1 = \frac{(\text{Fe}^{+2}) \text{H}(\text{nP})^{+1}}{(\text{Fe}(\text{nP})_3^{+2}) (\text{H}^{+1})^3} \quad (84)$$

and the equilibrium constant for Equation 83, K_2 , is

$$K_2 = \frac{(\text{Fe}^{+2}) (\text{H}_2(\text{nP})^{+2})^3}{(\text{Fe}(\text{nP})_3^{+2}) (\text{H}^{+1})^6} \quad (85)$$

The concentrations of the components in the equilibrium expression can be determined from the initial, total concentrations of HCl, Fe^{+2} and nP and the spectrophotometrically determined equilibrium concentration of $\text{Fe}(\text{nP})_3^{+2}$,

$$(\text{Fe}^{+2}) = (\text{Fe}_T^{+2}) - (\text{Fe}(\text{nP})_3^{+2}) \quad (86)$$

$$(\text{H}(\text{nP})^{+1}) = (\text{nP}_T) - 3(\text{Fe}(\text{nP})_3^{+2}) \quad (87)$$

$$(\text{H}^{+1}) = (\text{H}_T^{+1}) - x(\text{H}_x(\text{nP})^{+x}) \quad (88)$$

where for Equations 82 and 83 x equals 1 and 2 respectively.

Values of K_1 and K_2 were determined for a series of investigations at varying initial concentrations of HCl, Fe^{+2}

and nP. The results are listed in Table 15.

Table 15. Equilibrium study on 5-nitro-1,10-phenanthroline

Trial	H_T^{+1} $\underline{M} \times 10^5$	Fe_T^{+2} $\underline{M} \times 10^5$	nP_T $\underline{M} \times 10^5$	$Fe(nP)_3^{+2}$ $\underline{M} \times 10^5$	$K_1 \times 10^9$	$K_2 \times 10^4$
1	2.32	9.47	1.013	3.25	8.5	6840.0
2	10.43	9.47	1.013	2.55	36.5	300.0
3	83.4	9.47	1.013	0.32	38.2	0.7
4	41.7	9.47	3.039	5.25	35.2	5.0
5	83.4	9.47	10.13	9.05	33.3	0.6

The results show that in the study the values of K_2 varied over four orders of magnitude while the values for K_1 remained relatively constant. This indicates that Equation 82, that is, the dissociation of $Fe(nP)_3^{+2}$ to form $H(nP)^{+1}$, best describes the experimental system.

In another study the \bar{n} function was redefined to be the average number of hydrogen ions bound to the ligand, 5-nitro-1,10-phenanthroline,

$$\bar{n} = \frac{(H_T^{+1}) - (H^{+1})}{(nP_T)} \quad (89)$$

Experimental \bar{n} values were determined by preparing two solutions which both contained $1.579 \times 10^{-2} \underline{M}$ HCl. One of these solutions was prepared to contain $3.132 \times 10^{-3} \underline{M}$ 5-nitro-1,10-phenanthroline. In both solutions the medium was

30% acetonitrile in water to keep the sparingly soluble 5-nitro-1,10-phenanthroline in solution throughout the study. The two solutions were each titrated potentiometrically with $6.36 \times 10^{-2} \text{ M}$ KOH using the "Expanded Scale" on a Beckman Model GS potentiometer.

The concentration of uncombined hydrogen ion in the $\text{H}_x(\text{nP})^{+x}$ system, $(\text{H}^{+1})_{\text{P}}$, was determined from the following expression:

$$(\text{H}^{+1})_{\text{P}} = (\text{H}^{+1}) 10^{-\frac{(E-E_{\text{P}})}{59.15}} \quad (90)$$

where (H^{+1}) is the concentration of uncombined hydrogen ion in the titration of the solution which did not contain 5-nitro-1,10-phenanthroline, and E_{P} and E are the measured potentials of a glass electrode vs. the SCE in the titration of the solution which did and did not contain 5-nitro-1,10-phenanthroline respectively.

The values of \bar{n} in the $\text{H}_x(\text{nP})^{+x}$ titration could be determined from the experimental values of $(\text{H}^{+1})_{\text{P}}$ and the total concentrations of hydrogen ion and 5-nitro-1,10-phenanthroline using Equation 89. The values of \bar{n} approached but never exceeded a value of 1.0 which again indicates that $\text{H}(\text{nP})^{+1}$ and not $\text{H}_2(\text{nP})^{+2}$ is formed in acidic solutions of 5-nitro-1,10-phenanthroline.

The results of these two studies indicate that although the slope of the solubility plot for 5-nitro-1,10-phenanthro-

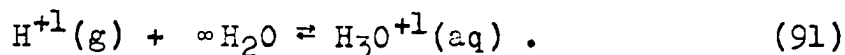
line is about 0.5, no $H_2(nP)^{+2}$ species appears to exist.

A value of \bar{n}_s for 5-nitro-1,10-phenanthroline was calculated from Equation 80 assuming that no higher order $H(nP)_n^{+1}$ species exist. The pK_a value reported by Brandt and Gullstrom (11) and a value of 4.1×10^{-4} M for the solubility of 5-nitro-1,10-phenanthroline in water, S_A^0 were used in the computation. A value of \bar{n}_s of 0.60 was calculated which agrees quite well with the experimental solubility slope value of 0.49.

In conclusion the $H(nP)^{+1}$ system does not appear to be unique compared to that for the other 1,10-phenanthrolines. Its low solubility slope appears to be a consequence of the low basicity and low aqueous solubility of the ligand.

VI. STRUCTURAL PROPOSAL

The hydrogen ion or bare proton is unique among other common ions in that it has no external electrons to shield or screen its positively charged nucleus. Further, its small size (about 10^{-13} cm.) relative to atomic sizes (about 10^{-8} cm.) gives rise to a large charge to size ratio. Hence, the hydrogen ion rarely exists as such, except in gaseous ion beams, and it is invariably associated with other atoms or molecules in condensed phases. In water the hydrogen ion is hydrated to form the hydronium ion, H_3O^{+1} ,



The energy of hydration for the formation of this strong covalent bond has been estimated to be about 283 kcal./mole (5b).

Evidence for the existence of the pyramidal H_3O^{+1} ion in solid hydrates of strong acids has been obtained by a variety of techniques, including NMR, IR and Raman spectrometry. For a summary of these techniques and a more detailed discussion of the hydronium ion the book by Bell (8) and the review article by Clever (12) would be useful.

Further hydration of the H_3O^{+1} ion was first proposed in 1954 by Wicke, Eigen and Ackermann (66). Using a model proposed by Eucken (18) from which ionic hydration numbers may be estimated from the temperature dependence of apparent molal quantities, Wicke et al. (66) have estimated a hydration

number of four for the hydrogen ion from the contribution by hydrogen ion to the partial molal heat capacity of hydrochloric acid in aqueous solution. The authors have proposed a pyramidal structure for the trihydrated hydronium ion, $\text{H}_3\text{O}^{+1}(\text{H}_2\text{O})_3$ or $\text{H}^{+1}(\text{H}_2\text{O})_4$ or $\text{H}_9\text{O}_4^{+1}$.

The subsequent literature is replete with other experimental evidence by a variety of techniques supporting the existence of the $\text{H}_9\text{O}_4^{+1}$ ion. It has also been used to explain a host of observed properties of aqueous strong acid solutions (12). A sampling of these studies will be summarized below.

Tuck and Diamond (61) have studied the solvent extraction of perchloric acid into the moderately basic solvents, dibutyl Cellosolve and diisopropyl ketone, and the extraction of perchloric, hydrochloric and hydrobromic acids into the more basic solvent, tri-n-butyl phosphate, TBP. They report that four molecules of water accompany each molecule of acid into the nonaqueous phase. They suggest that all four molecules of water are associated with the hydrogen ion forming the $\text{H}_9\text{O}_4^{+1}$ ion.

Knewstubb and Tickner (30) have investigated the mass spectrometry of ions formed in the negative glow and Faraday dark space of discharges in water vapor and have observed ions of the type, $\text{H}_3\text{O}^{+1}(\text{H}_2\text{O})_n$, where $n = 0$ to 5. Their data indicates that the bond strength of the ion falls off sharply after $n = 3$ and that the $\text{H}_9\text{O}_4^{+1}$ ion represents a particularly

stable species.

Gluekauf and Kitt (22) have reported values for the hydration number of cations determined from the adsorption of water by polystyrene sulphonates of cations using an isopiestic method. They report a value of four for the hydration number of the hydrogen ion.

Gluekauf (21) using a refinement of an earlier treatment by Stokes and Robinson (56) has developed an expression to determine the mean activity coefficient of concentrated electrolytes. From this treatment values of the hydration number for the ions can be estimated. His value for the hydration number of the hydrogen ion is also four.

Bascombe and Bell (5a) and Wyatt (67) have pointed out that a consideration of the Hammett acidity function can be used to determine the hydration number of the hydrogen ion. A value of four was obtained by both workers.

It is proposed that because of the unique charge distribution of the hydronium ion, a charge of about $+1/3$ is concentrated on each of the three hydrogen atoms, the hydronium ion may be expected to form strong hydrogen bonds binding one molecule of water to each of the three hydrogen atoms forming $\text{H}_3\text{O}^{+1}(\text{H}_2\text{O})_3$. Grahn (23) has estimated the strength of these three hydrogen bonds to be about 45 kcal./mole per bond. The three hydrogen bonded water molecules make up the primary hydration sphere of the hydronium ion. Additional hydration

should be possible in the secondary and outer hydration spheres. These outer hydrogen bonds would be expected to be considerably weaker than those in the inner, primary hydration sphere. Grahn (23) has estimated that the water molecules in the secondary hydration sphere are hydrogen bonded to the HgO_4^{+1} ion with a bond strength of about 9 kcal./mole and Azzam (5) has suggested that there are about nine water molecules in the secondary hydration sphere.

Tuck (59) has suggested that the structure of the HgO_4^{+1} ion is such that a maximum of three large, moderately basic organic molecules can hydrogen bond to it. The species, $(\text{TBP})_3\text{HgO}_4\text{X}$, has been characterized in the solvent extraction of the tetrachloroaurate(III) ion, X, from hydrochloric acid solution into a benzene solution containing tri-n-butyl phosphate, TBP, (60); and in the extraction of chromium(VI) from acidic solution into TBP in cyclohexane (62).

Whitney and Diamond (65) have studied the extraction of perchloric acid into solutions of TBP in inert solvents. They suggest that when the concentration of TBP in the inert solvent is low, the extracted species is $3\text{TBP}\cdot\text{H}_3\text{O}^{+1}\dots\text{ClO}_4^{-1}$ and when the concentration of TBP is high, the extracted species is $3\text{TBP}\cdot\text{HgO}_4^{+1}\dots\text{ClO}_4^{-1}$.

Upon considering the solvent extraction work by Tuck (59) and Whitney and Diamond (65) and the 1,10-phenanthroline-1-water studies by Smith and Richter (54), Fritz et al. (19) and Beattie and Webster (7), an idea about the possible structure

of the HP_n^{+1} species was formulated. Certainly an octahedral arrangement of three molecules of 1,10-phenanthroline about a hydrogen ion, analogous to the structure of FeP_3^{+2} , is highly unlikely since the hydrogen ion would not have suitable orbitals available to form this type of complex.

However, in the highest concentrations of 1,10-phenanthroline, it is possible that 1,10-phenanthroline could compete with and replace the water molecules in the secondary hydration sphere about the hydronium ion. Hence, it is proposed that $\text{HP}_n^{+1} = n\text{P} \cdot \text{H}_9\text{O}_4^{+1}$. The proposed structure for $3\text{P} \cdot \text{H}_9\text{O}_4^{+1}$ is shown in Figure 17.

It is also possible that the replacement of the water molecules by 1,10-phenanthroline could take place in the primary hydration sphere instead of the secondary hydration sphere. In this case the HP_n^{+1} species would be represented by, $\text{HP}_n^{+1} = n\text{P} \cdot \text{H}_3\text{O}^{+1}(3-n)\text{H}_2\text{O}$. A Fisher-Taylor-Hirschfelder molecular model of the hydronium ion was constructed and a molecule of 1,10-phenanthroline could be arranged about each of the hydrogen atoms of the hydronium ion.

However, this latter proposal seems to be less favorable than the former proposal. The type of bonding in the $n\text{P} \cdot \text{H}_9\text{O}_4^{+1}$ proposal would seem to better fit in with the type of bonding proposed in the 1,10-phenanthroline-1-water studies (7,19,54).

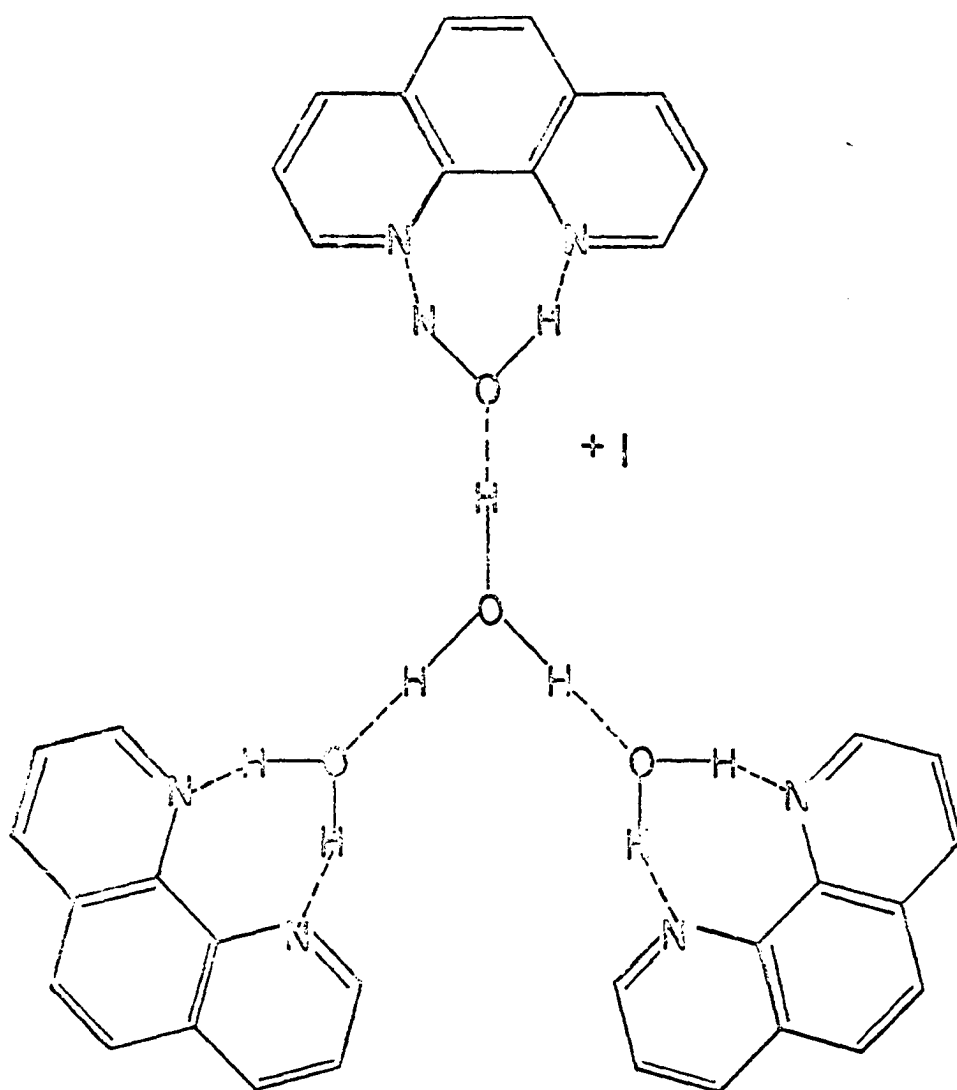


Figure 17. Proposed structure of HP_3^{+1} , $3P \cdot H_9O_4^{+1}$

VII. SUMMARY

The Ag/AgP₂NO₃ electrode, which was devised by Grimes (24) and further studied by Fullerton (20), has been used in the determination of the over-all stoichiometric formation constants of the hydrogen-, cadmium- and zinc-1,10-phenanthroline complexes. The values of β_n for the ZnP_n⁺² complexes determined in this study agree very well with those reported by the other workers. The value of β_1 reported by Dale (13) seems a little high compared to the other values and the value of β_3 reported by McClure (42) is considerably lower than the other reported values.

The values of β_n for the CdP_n⁺² complexes determined in the present study agree well with those reported by other workers. The value of β_3 agrees best with that obtained by Douglas et al. (16) from polarographic measurements but the value is somewhat higher than those reported by the other workers.

The values of β_n for the higher order HP_n⁺¹ species determined in this work are considerably lower than those reported by Grimes (24) and Fullerton (20). This is undoubtedly due to the manner in which the potentiometric study was conducted. Grimes (24) and Fullerton (20) used the Ag/AgP₂NO₃ electrode in a direct potentiometric technique based on a Nernstian electrode response. Therefore in their studies of the alkali metal-1,10-phenanthroline systems they

would have interpreted the lower, non-Nernstian slope of the electrode as an indication of complex formation of the alkali metals by 1,10-phenanthroline. For the same reason their values of β_n for the HP_n^{+1} species would be higher than those determined in the present work. It has been shown in this work and in the work by Dale (14) that the values of β_n for the KP_n^{+1} system are indeed excessive. The confidence in the values of β_n for the HP_n^{+1} species determined in this work was enhanced when these values were used to explain the experimental results for the solubility of 1,10-phenanthroline as a function of the total concentration of hydrochloric acid.

The formation function and degree of formation curves for the HP_n^{+1} system indicate why other workers have not detected the higher order HP_n^{+1} species. The system is dominated by the HP^{+1} species and the higher order species become significant only when the concentration of uncombined 1,10-phenanthroline is relatively high. The fraction of the total, 1,10-phenanthroline in the form of the higher order species is also directly dependent upon the total concentration of hydrogen ion.

It was previously noted that most workers have determined the acid dissociation constant of HP^{+1} by a pH technique. In the present work it was shown that in the potentiometric titration of 1,10-phenanthroline with a strong acid, the pH of the system is only slightly different when one considers

all three HP_n^{+1} species as compared to the case where only the HP^{+1} species is considered. Hence, the higher order HP_n^{+1} species would easily have gone unnoticed.

The potentiometric method used by Dale (13) has considerable merit in the study of metal-1,10-phenanthroline systems. However, the potentiometric method used in the present work is somewhat more convenient to use in that the concentration of uncombined 1,10-phenanthroline is obtained directly from the experimental Ag/AgP_2NO_3 electrode potential. In the method used by Dale (13) the concentration of uncombined 1,10-phenanthroline is calculated from the experimental, potentiometric measurement of the concentration of uncombined competing metal, silver(I), and the previously determined over-all formation constants of the AgP_n^{+1} complexes. Further, the method used in the present study seems to be better suited for studying metal-1,10-phenanthroline systems, like the HP_n^{+1} system, which have formation constants that are considerably lower than those for the AgP_n^{+1} complexes.

The weighted least squares computer program used in the determination of the over-all formation constants is a tremendous asset to a study of this nature. The program is objective in that all the experimental data from a metal-ligand system is treated simultaneously. This is in contrast to the graphical techniques which are often used to determine formation constants.

The solubility study used in this work was very helpful in elucidating the HP_n^{+1} system. It is a rapid and useful method for determining the maximum value of \bar{n} that may be attained in the HP_n^{+1} systems for 1,10-phenanthroline and the substituted 1,10-phenanthrolines. This maximum value of \bar{n} is an indication of the number of species that should be considered in the HP_n^{+1} systems. The solubility method would seem to be of general utility in the investigation of other metal-ligand systems where the ligand is only sparingly soluble.

The purpose of this work was to investigate the reaction between hydrogen ion and 1,10-phenanthroline to elucidate the novel higher order HP_n^{+1} species proposed by Grimes (24) and Fullerton (20). The evidence obtained from the potentiometric, solubility and infrared studies indicate that these unique species do exist. The structural proposals for the HP_n^{+1} species seem to fit in well with the recent developments concerning the $H_9O_4^{+1}$ species particularly the solvent extraction work by Tuck (59) and Whitney and Diamond (65) and the 1,10-phenanthroline-1-water work by Smith and Richter (54), Fritz et al. (19) and Beattie and Webster (7).

VIII. SUGGESTIONS FOR FUTURE WORK

- 1) It would be of interest to undertake a potentiometric study with the $\text{Ag}/\text{AgP}_2\text{NO}_3$ electrode to determine the formation constants of the HP_n^{+1} species in a mixed-solvent system where the solubility of 1,10-phenanthroline, and therefore the maximum value of \bar{n} that could be attained, would be increased. A mixed-solvent system which is principally aqueous would be recommended, perhaps dioxane-water. A study of the solubility of 1,10-phenanthroline as a function of the total concentration of acid in the proposed solvent system would be a rapid and easy way to evaluate the solvent system.
- 2) A partition study similar to that employed by Irving and Mellor (27) to determine the concentration of uncombined 1,10-phenanthroline would be an independent way to study the HP_n^{+1} system. The weighted least squares computer program could be used to determine the formation constants from the experimental data.
- 3) A study of the HP_n^{+1} systems of some substituted 1,10-phenanthrolines by a potentiometric or a partition method would be of interest. The low aqueous solubility of most substituted 1,10-phenanthrolines would necessitate the use of a mixed-solvent system.
- 4) Tuck (59) and Whitney and Diamond (65) have proposed the species, $(\text{TBP})_3\text{H}_9\text{O}_4^{+1}\text{X}^{-1}$ and $3\text{TBP}\cdot\text{H}_3\text{O}^{+1}\dots\text{X}^{-1}$, as a result of some solvent extraction studies. Perhaps further evidence

concerning the HP_n^{+1} system could be obtained from the investigation of the extraction of a strong acid from an aqueous solution into an immiscible, inert solvent containing 1,10-phenanthroline.

5) It would be of interest to undertake a complete investigation of the HP_n^{+1} system by employing some of the following techniques: infrared spectrometry, nuclear magnetic resonance spectrometry, molecular weight measurement and mass spectrometry.

6) It would be of interest to investigate the ionic mobility, transport number and other electrochemical properties of solutions containing the HP_n^{+1} species.

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